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The ABC of DFT

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Definitions and notation

Coordinates

Position vector: $\mathbf{r} = (x, y, z), r = |\mathbf{r}|$.

Spin index: $\sigma = \uparrow$ or $\downarrow = \alpha$ or β .

Space-spin vector: $x = (\mathbf{r}, \sigma)$.

Sums: $\int dx = \sum_{\sigma} \int d^3r$

Operators

Kinetic energy: $\hat{T} = -\frac{1}{2} \sum_i^N \nabla_i^2$.

Potential energy: $\hat{V} = \hat{V}_{\text{ee}} + \hat{V}_{\text{ext}}$

Coulomb repulsion: $\hat{V}_{\text{ee}} = \frac{1}{2} \sum_{i \neq j}^N 1/|\mathbf{r}_i - \mathbf{r}_j|$.

External potential: $\hat{V}_{\text{ext}} = \sum_{i=1}^N v_{\text{ext}}(\mathbf{r}_i)$

Wavefunctions

Physical wavefunction: $\Psi[n](x_1 \dots x_N)$ has density n and minimizes $\hat{T} + \hat{V}_{\text{ee}}$

Kohn-Sham: $\Phi[n](x_1 \dots x_N)$ has density n and minimizes $\hat{T}$

$\Phi(x_1 \dots x_N) = \sum_p (-1)^p \phi_1(x_{p_1}) \dots \phi_N(x_{p_N})$

$\Phi(x_1 \dots x_N) = \sum_p (-1)^p \phi_1(x_{p_1}) \dots \phi_N(x_{p_N})$

where $\phi_i(x)$ and ϵ_i are the i -th KS orbital and energy, with $i = \alpha\sigma$, with α =spatial orbital index.

Energies

Universal functional: $F[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{V}_{\text{ee}} | \Psi \rangle = \langle \Psi[n] | \hat{T} | \Psi[n] \rangle$

Kinetic energy: $T[n] = \langle \Psi[n] | \hat{T} | \Psi[n] \rangle$.

Non-interacting kinetic energy: $T_s[n] = \min_{\Phi \rightarrow n} \langle \Phi | \hat{T} | \Phi \rangle = \langle \Phi[n] | \hat{T} | \Phi[n] \rangle = \sum_{i=1}^N \int d^3r |\nabla \phi_i(\mathbf{r})|^2$

Coulomb repulsion energy: $V_{\text{ee}}[n] = \langle \Psi[n] | \hat{V}_{\text{ee}} | \Psi[n] \rangle$.

Hartree energy: $U[n] = \frac{1}{2} \int d^3r \int d^3r' n(\mathbf{r}) n(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|$

Exchange: $E_{\text{x}} = \langle \Phi | V_{\text{ee}} | \Phi \rangle - U = -\frac{1}{2} \sum_{\sigma} \sum_{i,j \text{ occ}} \int d^3r \int d^3r' \phi_{i\sigma}^*(\mathbf{r}) \phi_{j\sigma}^*(\mathbf{r}') \phi_{i\sigma}(\mathbf{r}) \phi_{j\sigma}(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|$

Kinetic-correlation: $T_{\text{c}}[n] = T[n] - T_s[n]$

Potential-correlation: $U_{\text{xc}}[n] = V_{\text{ee}}[n] - U[n]$

Exchange-correlation: $E_{\text{xc}}[n] = T[n] - T_s[n] + V_{\text{ee}}[n] - U[n] = \langle \Psi[n] | \hat{T} + \hat{V}_{\text{ee}} | \Psi[n] \rangle - \langle \Phi[n] | \hat{T} + \hat{V}_{\text{ee}} | \Phi[n] \rangle$

Potentials

Functional derivative: $F[n + \delta n] - F[n] = \int d^3r \delta n(\mathbf{r}) \delta F[n] / \delta n(\mathbf{r})$

Kohn-Sham: $v_{\text{s}}(\mathbf{r}) = -\delta T_{\text{s}} / \delta n(\mathbf{r}) + \mu$

Hartree: $v_{\text{H}}(\mathbf{r}) = \delta U / \delta n(\mathbf{r}) = \int d^3r' n(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|$

Exchange-correlation: $v_{\text{ext}}(\mathbf{r}) = v_{\text{s}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r})$

Densities and density matrices

Spin density: $n(x) = n_{\sigma}(\mathbf{r}) = N \int dx_2 \dots dx_N |\Psi(x, x_2, \dots, x_N)|^2 = \sum_{i=1}^N |\phi_i(x)|^2$

properties: $n(x) \geq 0$, $\int dx n(x) = N$

Density matrix: $\gamma(x, x') = N \int dx_2 \dots \int dx_N \Psi^*(x, x_2, \dots, x_N) \Psi(x', x_2, \dots, x_N)$

properties: $\gamma(x, x) = n(x)$, $\gamma(x', x) = \gamma(x, x')$

kinetic energy: $T = -\frac{1}{2} \int d^3r \nabla^2 \gamma(\mathbf{r}, \mathbf{r}')|_{\mathbf{r}=\mathbf{r}'}$

Kohn-Sham: $\gamma_s(x, x') = \delta_{\sigma\sigma'} \sum_{i=1}^{N_\sigma} \phi_{i\sigma}^*(\mathbf{r}) \phi_{i\sigma}(\mathbf{r}')$

Pair Density: $P(x, x') = N(N-1) \int dx_3 \dots \int dx_N |\Psi(x, x', x_3, \dots, x_N)|^2$

properties: $\int dx' P(x, x') = (N-1)n(x)$, $P(x', x) = P(x, x')$, $P(x, x') \geq 0$

potential energy: $V_{ee} = \frac{1}{2} \int d^3r \int d^3r' P(\mathbf{r}, \mathbf{r}')/|\mathbf{r} - \mathbf{r}'|$

Kohn-Sham: $P_x(x, x') = n(x)n(x') - |\gamma_s(x, x')|^2$

Exchange-correlation hole around $\mathbf{r}$ at coupling constant λ :

$P^\lambda(\mathbf{r}, \mathbf{r} + \mathbf{u}) = n(\mathbf{r}) [n(\mathbf{r} + \mathbf{u}) + n_{xc}^\lambda(\mathbf{r}, \mathbf{r} + \mathbf{u})]$

Kohn-Sham: $n_x(x, x') = -|\gamma_s(x, x')|^2/n(x)$

properties: $n_x(\mathbf{r}, \mathbf{r} + \mathbf{u}) \leq 0$, $\int d^3u n_x(\mathbf{r}, \mathbf{r} + \mathbf{u}) = -1$, $\int d^3u n_c^\lambda(\mathbf{r}, \mathbf{r} + \mathbf{u}) = 0$

Pair correlation function: $g^\lambda(x, x') = P^\lambda(x, x')/(n(x)n(x'))$

Electron-electron cusp condition: $dg^\lambda(\mathbf{r}, u)/du|_{u=0} = \lambda g^\lambda(\mathbf{r}, u=0)$

Uniform coordinate scaling

Density: $n(\mathbf{r}) \rightarrow n_\gamma(\mathbf{r}) = \gamma^3 n(\gamma\mathbf{r})$

Wavefunction: $\Psi_\gamma(\mathbf{r}_1 \dots \mathbf{r}_N) = \gamma^{3N/2} \Psi(\gamma\mathbf{r}_1 \dots \gamma\mathbf{r}_N)$

Ground states: $\Phi[n_\gamma] = \Phi_\gamma[n]$, but $\Psi[n_\gamma] \neq \Psi_\gamma[n]$

Fundamental inequality: $F[n_\gamma] \leq \gamma^2 T[n] + \gamma V_{ee}[n]$

Non-interacting kinetic energy: $T_s[n_\gamma] = \gamma^2 T_s[n]$

Exchange and Hartree energies: $E_x[n_\gamma] = \gamma E_x[n]$, $U[n_\gamma] = \gamma U[n]$

Kinetic and potential: $T[n_\gamma] < \gamma^2 T[n]$, $V_{ee}[n_\gamma] > \gamma V_{ee}[n]$ ($\gamma > 1$)

Correlation energies: $E_c[n_\gamma] > \gamma E_c[n]$, $T_c[n_\gamma] < \gamma^2 T_c[n]$ ($\gamma > 1$)

Virial theorem: $2T = \langle \mathbf{r} \cdot \nabla \hat{V} \rangle$

N electrons: $2T + V_{ee} = \int d^3r n(\mathbf{r}) \mathbf{r} \cdot \nabla v_{\text{ext}}(\mathbf{r})$

XC: $E_{xc} + T_c = \int d^3r n(\mathbf{r}) \mathbf{r} \cdot \nabla v_{xc}(\mathbf{r})$

Spin scaling

Kinetic: $T_s[n_\uparrow, n_\downarrow] = \frac{1}{2} (T_s[2n_\uparrow] + T_s[2n_\downarrow])$

Exchange: $E_x[n_\uparrow, n_\downarrow] = \frac{1}{2} (E_x[2n_\uparrow] + E_x[2n_\downarrow])$

Adiabatic connection

Hellmann-Feynman: $E = E^{\lambda=0} + \int_0^1 d\lambda \langle \Psi^\lambda | dH^\lambda / d\lambda | \Psi^\lambda \rangle$

Wavefunction: $\Psi^\lambda[n]$ has density n and minimizes $\hat{T} + \lambda \hat{V}_{ee}$;

relation to scaling: $\Psi^\lambda[n] = \Psi_\lambda[n_{1/\lambda}]$

Energies: $E^\lambda[n] = \lambda^2 E[n_{1/\lambda}]$

kinetic: $T_s^\lambda[n] = T_s[n]$

exchange: $E_x^\lambda[n] = \lambda E_x[n]$, $U^\lambda[n] = \lambda U[n]$

correlation: $E_c^\lambda[n] = \lambda^2 E_c[n_{1/\lambda}] = \lambda^2 \{E_c^{(2)}[n] + \lambda E_s^{(3)}[n] + \dots\}$ for small λ

ACF: $E_{xc} = \int_0^1 d\lambda U_{xc}(\lambda)$, where $U_{xc}(\lambda) = U_{xc}^\lambda/\lambda$

Finite systems

Kato's cusp at nucleus: $dn/dr|_{\mathbf{r}=\mathbf{R}_\alpha} = -2Z_\alpha n(\mathbf{R}_\alpha)$

Large r in Coulombic system: $\sqrt{n(\mathbf{r})} \rightarrow Ar^\beta e^{-\sqrt{2I}r}$, $\beta = \sum_\alpha Z_\alpha - N + 1/\sqrt{2I}$

Exchange potential: $v_x(\mathbf{r}) \rightarrow -1/r$

Correlation potential: $v_c(\mathbf{r}) \rightarrow -\alpha(N-1)/2r^4$, where $\alpha(N-1)$ is the polarizability of the $N-1$ electron system.

Von-Weisacker: $T_s^{\text{VW}}[n] = \int d^3r |\nabla n|^2/(8n)$ (exact for $N=1,2$)

Exchange: $E_x = -U/N$ for $N=1,2$

Correlation: $E_c = 0$ for $N=1$

High-density limit: $E_c[n_\gamma] = E_c^{(2)}[n] + E_c^{(3)}[n]/\gamma + \dots$ as $\gamma \rightarrow \infty$

Low-density limit: $E_c[n_\gamma] = \gamma B[n] + \gamma^{3/2} C[n] + \dots$ as $\gamma \rightarrow 0$.

Uniform gas and LSD

Measures of the local density Wigner-Seitz radius: $r_s(\mathbf{r}) = (3/(4\pi n(\mathbf{r})))^{1/3}$

Fermi wave vector: $k_F(\mathbf{r}) = (3\pi^2 n(\mathbf{r}))^{1/3}$

Thomas-Fermi wavevector: $k_s(\mathbf{r}) = \sqrt{4k_F(\mathbf{r})/\pi}$

Measure of the local spin-polarization:

Relative polarization: $\zeta(\mathbf{r}) = (n_\uparrow(\mathbf{r}) - n_\downarrow(\mathbf{r}))/n(\mathbf{r})$

Kinetic energy: $t_s^{\text{unif}}(n) = (3/10)k_F^2(n)n$

exchange energy: $e_x^{\text{unif}}(n) = n\epsilon_x^{\text{unif}}(n)$, where $\epsilon_x^{\text{unif}}(n) = (3k_F(n)/4\pi)$,

correlation energy: $\epsilon_c^{\text{unif}}(r_s) \rightarrow 0.0311 \ln r_s - 0.047 + 0.009r_s \ln r_s - 0.017r_s$ ($r_s \rightarrow 0$)

Thomas-Fermi: $T_s^{\text{TF}}[n] = A_s \int d^3r n^{5/3}(\mathbf{r})$ where $A_s = 2.871$.

LSD: $E_x^{\text{LDA}}[n] = A_x \int d^3r n^{4/3}(\mathbf{r})$ where $A_x = -(3/4)(3/\pi)^{1/3} = -0.738$.

$E_c^{\text{LSD}}[n_\uparrow, n_\downarrow] = \int d^3r n(\mathbf{r})\epsilon_c^{\text{unif}}(r_s(\mathbf{r}), \zeta(\mathbf{r}))$

Gradient expansions

Gradient expansion: $A[n] = \int d^3r \{a(n(\mathbf{r})) + b(n(\mathbf{r})|\nabla n(\mathbf{r})|^2 \dots\}$

Gradient expansion approximation: $A^{\text{GEA}}[n] = A^{\text{LDA}}[n] + \Delta A^{\text{GEA}}[n]$

Reduced density gradient: $s(\mathbf{r}) = |\nabla n(\mathbf{r})|/(2k_F(\mathbf{r})n(\mathbf{r}))$

Correlation gradient: $t(\mathbf{r}) = |\nabla n(\mathbf{r})|/(2k_s(\mathbf{r})n(\mathbf{r}))$

Polarization enhancement: $\phi(\zeta) = ((1+\zeta)^{2/3} + (1-\zeta)^{2/3})/2$

Kinetic energy: $T_s[n] = A_s \int d^3r n^{5/3}(1 + 5s^2/27)$ or $\Delta T_s^{\text{GEA}}[n] = T^{\text{VW}}[n]/9$.

Exchange energy: $E_x[n] = A_x \int d^3r n^{4/3}(1 + 10s^2/81)$

High-density correlation energy: $\Delta E_c^{\text{GEA}} = (2/3\pi^2) \int d^3r n(\mathbf{r})\phi(\zeta(\mathbf{r}))t^2(\mathbf{r})$

Generalized gradient approximation: $A^{\text{GGA}}[n] = \int d^3r a(n, |\nabla n|)$

Enhancement factor: $E_{xc}^{\text{GGA}} = \int d^3r e_x^{\text{unif}}(n(\mathbf{r})) F_{xc}(r_s(\mathbf{r}), s(\mathbf{r}))$

Chapter 1

Overview and elementary example

1.1 Importance of density functional theory to modern chemistry and materials modelling

¹ Density functional theory (DFT) has long been the mainstay of electronic structure calculations in solid-state physics, and has recently become popular in quantum chemistry. This is because present-day approximate functionals provide a useful balance between accuracy and computational cost, allowing much larger systems to be treated than traditional *ab initio* methods, while retaining much of their accuracy. Nowadays, traditional wavefunction methods, either variational or perturbative, can be applied to find highly accurate results on smaller systems, providing benchmarks for developing density functionals, which can then be applied to much larger systems

But DFT is not just another way of solving the Schrödinger equation. Nor is it a method of parametrizing empirical results. Density functional theory is a completely different, formally rigorous, way of approaching *any* interacting problem, by mapping it *exactly* to a much easier-to-solve non-interacting problem. Its methodology is applied in a large variety of fields to many different problems, with the ground-state electronic structure problem simply being the most ubiquitous.

The aim of this course is to provide a relatively gentle, but nonetheless rigorous, introduction to this subject. The technical level is no higher than any graduate quantum course, but leaps at the conceptual level are required, almost as large as those in going from classical to quantum mechanics. Students from all areas are invited to work through the material. The only necessary requirements are a good background in elementary quantum mechanics, no fear of calculus of more than one variable, and a deep desire to learn. You should end up knowing what the Kohn-Sham equations are, what functionals are, how much (or little) is known of their exact properties, how they can be approximated, and how insight into all these things produces understanding of the errors in electronic structure calculations. The hope is that these notes will be used by students worldwide to

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gain a better understanding of this fundamental theory. I ask only that you send me an email (to kieron@rutchem.rutgers.edu) if you use this material. In return, I am happy to grade problems and answer questions for all who are interested. These notes are copyright of Kieron Burke. No reproduction for purposes of sale is allowed.

Throughout the text, there are exercises that must be performed to get full value from the book. Also, at the end of each chapter, there are questions aimed at making you think about the material. These should be answered, but answers don't need to be written out as explicitly as for the problems.

1.2 What is a Kohn-Sham calculation?

To give an idea of what DFT is all about, and why it is so useful, we start with a very simple example, the hydrogen molecule, H_2 . Throughout this book, we will make the Born-Oppenheimer approximation, in which we treat the heavy nuclei as fixed points, and we want only to solve the ground-state quantum mechanical problem for the electrons.

In regular quantum mechanics, we must solve the Schrödinger equation:

$$\left\{ -\frac{1}{2} \sum_{i=1,2} \nabla_i^2 + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + \sum_{i=1,2} v_{\text{ext}}(\mathbf{r}_i) \right\} \Psi(\mathbf{r}_1, \mathbf{r}_2) = E \Psi(\mathbf{r}_1, \mathbf{r}_2), \quad (1.1)$$

where the index i runs over the two electrons, and the external potential, the potential experienced by the electrons due to the nuclei, is

$$v_{\text{ext}}(\mathbf{r}) = -Z/r - Z/|\mathbf{r} - R\hat{\mathbf{z}}|, \quad (1.2)$$

where $Z = 1$ is the charge on each nucleus, $\hat{\mathbf{z}}$ is a unit vector along the bond axis, and R is a chosen internuclear separation. Except where noted, we use atomic units throughout this text, so that

$$e^2 = \hbar = m = 1, \quad (1.3)$$

where e is the electronic charge, $\hbar$ is Planck's constant, and m is the electronic mass. In consequence, all energies are in Hartrees $1 H = 27.2114 \text{ eV} = 627.5 \text{ kcal/mol}$ and all distances are given in Bohr radii $a_o = 0.529 \text{ \AA}$. In this example, the electrons are in a spin singlet, so that their spatial wavefunction $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ is symmetric under interchange of $\mathbf{r}_1$ and $\mathbf{r}_2$. Solution of Eq. (1.1) is complicated by the electrostatic repulsion between the particles, which we denote as V_{ee} . It couples the two coordinates together, making Eq. (1.1) a complicated partial differential equation in 6 coordinates, and its exact solution can be quite demanding. In Fig. 1.1 we plot the results of such a calculation for the total energy of the molecule, $E + 1/R$, the second term being the Coulomb repulsion of the nuclei. The position of the minimum is the equilibrium bond length, while the depth of the minimum, minus the zero point vibrational energy, is the bond energy. More generally, the global energy minimum determines all the geometry of a molecule, or the lattice

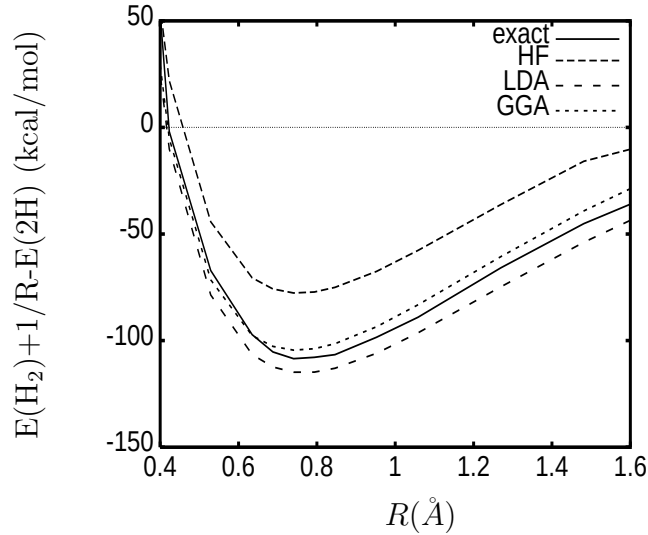


Figure 1.1: The total energy of the H_2 molecule as a function of internuclear separation.

structure of a solid, as well as all the vibrations and rotations. But for larger systems with N electrons, the wavefunction depends on all $3N$ coordinates of those electrons.

We note at this point that, with an exact ground-state wavefunction, it is easy to calculate the probability density of the system:

$$n(\mathbf{r}) = 2 \int d^3r' |\Psi(\mathbf{r}, \mathbf{r}')|^2. \quad (1.4)$$

The probability density tells you that the probability of finding an electron in d^3r around $\mathbf{r}$ is $n(\mathbf{r})d^3r$. For our H_2 molecule at equilibrium, this would look like the familiar two decaying exponentials centered over the nuclei, with an enhancement in between, where the chemical bond has formed.

Next, imagine a system of two *non-interacting* electrons in some potential, $v_s(\mathbf{r})$, chosen somehow to mimic the true electronic system. Because the electrons are non-interacting, their coordinates decouple, and their wavefunction is a simple product of one-electron wavefunctions, called *orbitals*, satisfying:

$$\left\{ -\frac{1}{2}\nabla^2 + v_s(\mathbf{r}) \right\} \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \quad (1.5)$$

where $\Phi(\mathbf{r}_1, \mathbf{r}_2) = \phi_0(\mathbf{r}_1)\phi_0(\mathbf{r}_2)$. This is a much simpler set of equations to solve, since it only has 3 coordinates. Even with many electrons, say N , one would still need to solve only a 3-D equation, and then occupy the first $N/2$ levels, as opposed to solving a $3N$ -coordinate Schrödinger equation. If we can get our non-interacting system to accurately 'mimic' the true system, then we will have a computationally much more tractable problem to solve.

How do we get this mimicking? Traditionally, if we think of approximating the true wavefunction by a non-interacting product of orbitals, and then minimize the energy, we

find the Hartree-Fock equations, which yield an effective potential:

$$v_s^{\text{HF}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \frac{1}{2} \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (1.6)$$

The correction to the external potential mimics the effect of the second electron, in particular screening the nuclei. For example, at large distances from the molecule, this potential decays as $-1/r$, reflecting an effective charge of $Z-1$. Note that insertion of this potential into Eq. (1.5) now yields a potential that depends on the electronic density, which in turn is calculated from the solution to the equation. This is termed therefore a self-consistent set of equations. An initial guess might be made for the potential, the eigenvalue problem is then solved, the density calculated, and a new potential found. These steps are repeated until there is no change in the output from one cycle to the next – self-consistency has been reached. Such a set of equations are often called self-consistent field (SCF) equations. In Fig. 1.1, we plot the Hartree-Fock result and find that, although its minimum position is very accurate, it underbinds the molecule significantly. This has been a well-known deficiency of this method, and traditional methods attempt to improve the wavefunction to get a better energy. The missing piece of energy is called the correlation energy.

In a Kohn-Sham calculation, the basic steps are very much the same, but the logic is entirely different. Imagine a pair of non-interacting electrons which have precisely the same density $n(\mathbf{r})$ as the physical system. This is the Kohn-Sham system, and using density functional methods, one can derive its potential $v_s(\mathbf{r})$ if one knows how the total energy E depends on the density. A single simple approximation for the unknown dependence of the energy on the density can be applied to all electronic systems, and predicts both the energy and the self-consistent potential for the fictitious non-interacting electrons. In this view, the Kohn-Sham wavefunction of orbitals is *not* considered an approximation to the exact wavefunction. Rather it is a precisely-defined property of any electronic system, which is determined uniquely by the density. To emphasize this point, consider our H_2 example in the united atom limit, i.e., He. In Fig. 1.2, a highly accurate many-body wavefunction for the He atom was calculated, and the density extracted. In the bottom of the figure, we plot both the physical external potential, $-2/r$, and the *exact* Kohn-Sham potential. Two non-interacting electrons sitting in this potential have precisely the same density as the interacting electrons. If we can figure out some way to approximate this potential accurately, we have a much less demanding set of equations to solve than those of the true system. Thus we are always trying to improve a non-interacting calculation of a non-interacting wavefunction, rather than that of the full physical system. In Fig. 1.1 there are also plotted the local density approximation (LDA) and generalized gradient approximation (GGA) curves. LDA is the simplest possible density functional approximation, and it already greatly improves on HF, although it typically overbinds by about 1/20 of a Hartree (or 1 eV or 30 kcal/mol), which is too inaccurate for most quantum chemical purposes, but sufficiently reliable for many solid-state calculations. More sophisticated GGA's (and hybrids) reduce the typical error in LDA by about a factor of 5 (or

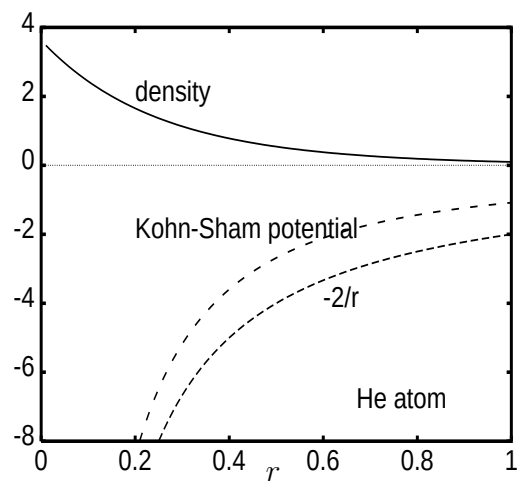


Figure 1.2: The external and Kohn-Sham potentials for the He atom, thanks to Cyrus’ Umrigar’s very accurate density.

more), making DFT a very useful tool in quantum chemistry. In section 1.4, we show how density functionals work with a simple example from elementary quantum mechanics.

1.3 Reinterpreting molecular orbitals

The process of bonding between molecules is shown in introductory chemistry textbooks as linear combinations of atomic orbitals forming molecular orbitals of lower energy, as in Fig.

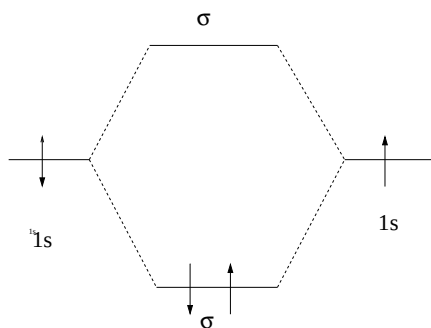


Figure 1.3: Orbital diagram of H_2 bond formation.

But later, in studying computational chemistry, we discover this is only the Hartree-Fock picture, which, as stated above, is rarely accurate enough for quantum chemical

calculations. In this picture, we need a more accurate wavefunction, but then lose this simple picture of chemical bonding. This is a paradox, as chemical reactivity is usually thought of in terms of frontier orbitals.

In the Kohn-Sham approach, the orbitals are *exact* and *unique*, i.e., there exists (at most) one external potential that, when doubly occupied by two non-interacting electrons, yields the exact density of the H_2 molecule. So in this view, molecular orbital pictures retain their significance, if they are the exact Kohn-Sham orbitals, rather than those of Hartree-Fock. And a highly accurate approximate density functional calculation produces the full electronic energy from these orbitals, resolving the paradox.

1.4 Simple example: Kinetic energy in one dimension

In general, we write our Hamiltonian as

$$\hat{H} = \hat{T} + \hat{V} \quad (1.7)$$

where $\hat{T}$ denotes the operator for the kinetic energy and $\hat{V}$ the potential energy. We begin with the simplest possible case. The Hamiltonian for a 1-D 1-electron system can be written as

$$\hat{H} = -\frac{1}{2} \frac{d^2}{dx^2} + V(x) \quad (1.8)$$

The time-independent Schrödinger equation has solutions:

$$\hat{H}\phi_i = \varepsilon_i\phi_i, \quad i = 0, 1, \dots \quad (1.9)$$

Thus ε_0 denotes the ground state energy and ϕ_0 the ground state wave function. Because the operator $\hat{H}$ is hermitian the eigenstates can be chosen orthonormal:

$$\int_{-\infty}^{\infty} dx \phi_i^*(x) \phi_j(x) = \delta_{ij} \quad (1.10)$$

Thus each eigenfunction is normalized. The electron probability density is just $n(x) = |\phi_0(x)|^2$.

Exercise 1 Particle in a one-dimensional box

Consider the elementary example of a particle in a box, i.e., $V(x) = \infty$ everywhere, except $0 \leq x \leq L$, where $V = 0$. This problem is given in just about all elementary textbooks on quantum mechanics. Show that the solution consists of trigonometric functions (standing waves), and making them vanish at the boundaries quantizes the energy, i.e.,

$$\phi_i = \sqrt{\frac{2}{L}} \sin(k_i x), \quad i = 1, 2, \dots \quad (1.11)$$

where $k_i = \pi i/L$, and the energies are $\varepsilon_i = k_i^2/2$. Check the orthonormality condition, Eq. (1.10).

Next we consider the following approximate *density functional* for the kinetic energy of non-interacting electrons in one-dimension. Don't worry if you never heard of a functional before. In fact, chapter 2 discusses functionals in some detail. For now, we need only the fact that a functional is a rule which maps a function onto a number. We use square brackets $[..]$ to indicate a functional dependence. The functional we write down will be the local approximation to the kinetic energy of non-interacting spinless fermions in one dimension. We do not derive it here, but present it for calculational use, and derive it later in the course:

$$T_s^{\text{loc}}[n] = 1.645 \int_{-\infty}^{\infty} dx n^3(x). \quad (1.12)$$

A *local* functional is one which is a simple integral over a function of its argument. Now, since for the particle in a box, all its energy is kinetic, we simply estimate the energy using $T_s^{\text{loc}}[n]$. Since the electron density is the square of the orbital:

$$n_1(x) = \frac{2}{L} \sin^2(k_1 x), \quad (1.13)$$

we find $T_s^{\text{loc}} = 4.11/L^2$, a 17% underestimate of the true value, $\pi^2/2L^2 = 4.93/L^2$. What is so great about that? There is not much more work in finding the exact energy (just take the second derivative of ϕ_1 , and divide by ϕ_1) as there is in evaluating the integral.

But watch what happens if there are two particles, fermions of the same spin (the general case for which T_s^{loc} was designed). We find now $E = \epsilon_1 + \epsilon_2 = 5\pi^2/2L^2 = 24.7/L^2$. If we evaluate the approximate kinetic energy again, using $n(x) = n_1(x) + \frac{2}{L} \sin^2(k_2 x)$, we find $T_s^{\text{loc}} = 21.8/L^2$, an 11% underestimate.

Exercise 2 Three particles in a box

Calculate the exact energy of three identical fermions in a box of length L . Plot the total density for one, two, and three particles. Compare the exact energy with that from the local approximation. What happens as the number of electrons grows?

These results are gotten by the evaluation of a simple integral over the density, whereas the exact numbers require solving for *all* the eigenvalues of the box, up to N , the number of electrons in it. Thus approximate density functionals produce reliable but inexact results at a fraction of the usual cost.

To see how remarkable this is, consider another paradigm of textbook quantum mechanics, namely the one-dimensional harmonic oscillator. In the previous example, the particles were plane waves; in this one, they are Gaussians, i.e., of a completely different shape. Applying the same approximate functional, we find merely a 10% overestimate.

Exercise 3 Kinetic energy of 1-d harmonic oscillator

What is the ground-state energy of a 1-d harmonic oscillator? What is its kinetic energy? Calculate its density, and from it extract the local density approximation to its kinetic energy. Repeat for two electrons occupying the lowest two levels of the well.

Congratulations. You have performed your first elementary density functional calculations, and are well on the way to becoming an expert.

We will see, later in the course, how, if we had an extremely accurate non-interacting kinetic energy density functional in three dimensions, we could revolutionize electronic structure calculations, by making them very fast. This is because we would then have a method for calculating the density and ground-state energy of systems which involved solving a single self-consistent integro-differential equation for *any* electronic system. This would be a true density functional calculation. Most present calculations do not do this. By solving an effective single-particle equation for the orbitals (the Kohn-Sham equation), they find T_s exactly, but at large computational cost (for large systems). So now you even know an unsolved problem in density functional theory.

Now answer the following simple questions as well as you can, justifying your answers in each case.

1.5 Questions about overview

1. Why is a Kohn-Sham calculation much faster than a traditional wavefunction calculation?
2. If you evaluate the kinetic energy of a Kohn-Sham system, is it equal to the physical kinetic energy?
3. Repeat above question for $\langle 1/r \rangle$, which can be measured in scattering experiments.
4. Why is the density cubed in the local approximation for T_s ? (see section ?? for the answer).
5. If you hadn't been given it, what procedure would you use to determine the constant in T_s^{loc} ? (see section 5.2 for the answer).
6. In what way will T_s^{loc} change if spin is included, e.g., for two electrons of opposite spin in a box? (see section 6.2 for the answer).
7. If we add an infinitesimal to $n(x)$ at a point, i.e., $\epsilon\delta(x)$ as $\epsilon \rightarrow 0$, how does T_s^{loc} change? (see section 2.2 for the answer).
8. Suggest a simple correction to T_s^{loc} , hoping to make it more accurate. (see section 9.1 for the answer).
9. Can you find a one-electron problem for which T_s^{loc} does badly? Try.
10. Does $T_s^{\text{loc}}[n^*]$ work for a single electron in an excited state, with density $n^*(\mathbf{r})$?

Chapter 2

Functionals and how to minimize them

¹ In this chapter, we introduce in a more systematic fashion what exactly a functional is, and how to perform elementary operations on functionals. This mathematics will be needed when we describe the quantum mechanics of interacting electrons in terms of density functional theory.

2.1 What is a functional?

A function maps one number to another. A *functional* assigns a number to a function. For example, consider all functions $r(\theta)$, $0 \leq \theta \leq 2\pi$, which are periodic, i.e., $r(\theta + 2\pi) = r(\theta)$. Such functions describe shapes in two-dimensions of curves which do not “double-back” on themselves, such as in Fig. 2.1. For every such curve, we can define the perimeter P as

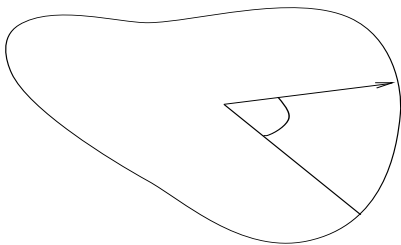


Figure 2.1: A 2D curve which is generated by a function $r = r(\theta)$

the length of the curve, and the area A as the area enclosed by it. These are *functionals* of $r(\theta)$, in the sense that, for a given curve, such as the ellipse

$$r(\theta) = 1/\sqrt{\sin^2(\theta) + 4 \cos^2(\theta)} \quad (2.1)$$

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there is a single well-defined value of P and of A . We write $P[r]$ and $A[r]$ to indicate this functional dependence. Note that, even if we don't know the relation explicitly, we do know it exists: Every bounded curve has a perimeter and an area.

For this simple example, we can use elementary trigonometry to deduce explicit formulas for these functionals. We simply consider the contribution from an infinitesimal change in angle $d\theta$, and integrate over the entire range of angles. Thus, in such a change, we have a contribution $r(\theta) \sin(d\theta) \approx r d\theta$ to the perimeter, yielding

$$P[r] = \int_0^{2\pi} d\theta r(\theta). \quad (2.2)$$

Similarly, the contribution to the area is that of a triangle of base $r \cos(d\theta) \approx r$ and height $r(\theta) \sin(d\theta) \approx r d\theta$, yielding

$$A[r] = \frac{1}{2} \int r d\theta r = \frac{1}{2} \int_0^{2\pi} d\theta r^2(\theta) \quad (2.3)$$

For an arbitrary $r(\theta)$ the integral above can be evaluated to give the area which is enclosed by the curve. Thus this functional maps a real function of one argument to a number, in this case the area enclosed by the curve.

Both of the above functionals are *local* functionals of $r(\theta)$, since they can be written in the form:

$$A[r] = \int_0^{2\pi} d\theta f(r(\theta)), \quad (2.4)$$

where $f(r)$ is a function of r . For P , $f = r$, while for A , $f = r^2/2$. These are called local because, inside the integral, one needs only to know the function right at a single point to evaluate the contribution to the functional from that point.

We have already come across a few examples of *density* functionals. In the opening chapter, the local approximation to the kinetic energy is a local functional of the density, with $f(n) = 1.645n^3$. For any one-electron system, the exact kinetic energy is given by the von Weisacker functional:

$$T_s^{\text{vw}}[n] = \int_{-\infty}^{\infty} dx \left(\frac{dn}{dx} \right)^2 / (8n)^2. \quad (2.5)$$

This is called a *semi-local* functional, because it depends on both the density and its gradient at any given point in space. Later we will give some examples of fully non-local functionals.

2.2 Functional derivatives

When we show that the ground-state energy of a quantum mechanical system is a functional of the density, we will then want to minimize that energy to find the true ground-state density. To do this, we must learn how to differentiate functionals, in much the same way as we learn how to differentiate regular functions in elementary calculus.

To begin with, we must define a functional derivative. Imagine making a tiny increase in a function, localized to one point, and asking how the value of a functional has changed due to this increase, i.e., we add an infinitesimal change $\delta r(\theta) = \epsilon \delta(\theta - \theta_0)$. How does $A[r]$ change?

$$A[r + \delta r] - A[r] = \frac{1}{2} \int_0^{2\pi} d\theta \left\{ (r + \epsilon \delta(\theta - \theta_0))^2 - r^2 \right\} = \int_0^{2\pi} d\theta r \epsilon \delta(\theta - \theta_0) = \epsilon r(\theta_0) \quad (2.6)$$

The functional derivative, denoted $\delta A / \delta r(\theta)$ is just the change in A divided by ϵ , or just $r(\theta)$ in this case. Since this is linear in the change in r , the general definition, for *any* infinitesimal change in r , is just

$$A[r + \delta r] - A[r] = \int_0^{2\pi} d\theta \frac{\delta A}{\delta r(\theta)} \delta r(\theta), \quad (2.7)$$

where the functional derivative $\delta A / \delta r(\theta)$ is that function of θ which makes this formula exact for any small change in $r(\theta)$. Just as the usual derivative df/dx of a function $f(x)$ tells you how much f changes when x changes by a small amount, i.e., $f(x + dx) - f(x) = (df/dx) dx + O(dx^2)$, so does the functional derivative, a function, tell you how much a functional changes when its arguments changes by a small “amount” (in this case, a small function). Applying similar reasoning to $P[r]$, we find

$$v[r](\theta) \equiv \frac{\delta A[r]}{\delta r(\theta)} = r(\theta), \quad \frac{\delta P[r]}{\delta r(\theta)} = 1, \quad (2.8)$$

where the notation $v[r](\theta)$ emphasizes that the functional derivative of $A[r]$ is a θ -dependent functional.

Exercise 4 Derivative of a local functional

Show that, for any local functional $A[n] = \int dx a(n(x))$, the functional derivative is $\delta A / \delta n(x) = a'(n(x))$, where $a'(n) = da/dn$.

In general, the way to find a functional derivative is to evaluate the expression $A[r + \delta r] - A[r]$ to leading order in δr , and the resulting integral must be cast in the form of a function times δr . Often it is necessary to do an integration by parts to identify the functional derivative.

Exercise 5 Derivative of a semilocal functional

Find the functional derivative of a semilocal functional $B[n] = \int_{-\infty}^{\infty} dx b(n, dn/dx)$, assuming n and its derivatives vanish rapidly as $|x| \rightarrow \infty$. Use your answer to show

$$\frac{\delta T_s^{\text{VW}}}{\delta n(x)} = -\frac{n''}{4n} + \frac{n'^2}{8n^2}. \quad (2.9)$$

The density functionals we use in practice are three-dimensional:

Exercise 6 Hartree potential

The Hartree (or classical electrostatic) energy of a charge distribution interacting with itself via Coulomb's law is given by

$$U[n] = \frac{1}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (2.10)$$

Find its functional derivative, the Hartree potential $v_H[n](\mathbf{r})$.

2.3 Euler-Lagrange equations

The last piece of functional technology we need for now is how to solve a constrained optimization problem, i.e., how to maximize (or minimize) one functional, subject to a constraint imposed by another.

For example, we might want to know what is the maximum area we can enclose inside a piece of loop of string of fixed length l . Thus we need to maximize $A[r]$, subject to the constraint that $P[r] = l$. There is a well-known method for doing such problems, called the method of Lagrange multipliers. Construct a new functional

$$B[r] = A[r] - \mu P[r], \quad (2.11)$$

where μ is at this point an unknown constant. Then extremize the new functional $B[r]$, by setting its functional derivative to zero:

$$\frac{\delta B}{\delta r} = \frac{\delta A}{\delta r} - \mu \frac{\delta P}{\delta r} = r(\theta) - \mu = 0, \quad (2.12)$$

or $r(\theta) = \mu$, a constant. This tells us that the optimum shape is a circle, and the radius of that circle can be found by inserting the solution in the constraint, $P[r = \mu] = 2\pi\mu = l$. The largest area enclosable by a piece of string of length l is $A[r = \mu] = l^2/(4\pi)$.

Exercise 7 One electron DFT

For one electron in one dimension, the total energy density functional is $E[n] = T_s^{\text{VW}}[n] + \int_{-\infty}^{\infty} dx v(x) n(x)$. Find the equation satisfied by the density which minimizes the energy, subject to the constraint that the density is normalized to 1.

Exercise 8 Change in a functional

Suppose you know that a functional $E[n]$ has functional derivative $v(r) = -1/r$ for the density $n(r) = Z \exp(-2Zr)$, where $Z = 1$. Estimate the change in E when Z becomes 1.1.

Exercise 9 Second functional derivative

Find the second functional derivative of (a) a local functional and (b) T_s^{VW} .

2.4 Questions about functionals

1. Compare the functional derivative of $T_s^{\text{VW}}[n]$ with $T_s^{\text{loc}}[n]$ for some sample one-electron problem. Comment.
2. If someone just tells you a number for any density you give them, e.g., the someone might be Mother Nature, and the number might be the total energy measured by experiment, devise a method for deducing if Mother Nature's functional is local or not.
3. Is there a simple relationship between T_s and $\int dx n(x) \delta T_s / \delta n(x)$? First check the local approximation, then Von Weisacker. Comment on your result.
4. For fixed particle number, is there any uncertainty in the functional derivative of a density functional?

Answers

1. You might take either the particle in the box or the harmonic oscillator or the one-dimensional hydrogen atom. You should find that a plot of the two functional derivatives gives you two very different curves in each case. To understand this, think of functions. Imagine one function being a horizontal line, and a second function having weak but rapid oscillations around that line. The second function is a good approximation to first everywhere, but its derivative is very different.
2. Take the second functional derivative. If its proportional to a delta function, the function is local. Note that just saying if the integrand depends only on the argument at $\mathbf{r}$ is not enough, since integrands can change within functionals by e.g., integrating by parts.
3. You should have found that the integral is three times the functional for the local approximation, but equal to the functional for von Weisacker. This would seem to be a failing of the local approximation, but see below to understand a bug in this question.
4. If the particle number does not change, then $\int d^3r \delta n(\mathbf{r}) = 0$. Thus addition of any constant to a functional derivative does not alter the result, so that the functional derivative is not determined up to a constant.

Chapter 3

Wavefunction quantum mechanics: From one to many electrons

¹ In this chapter, we review the traditional wavefunction picture of Schrödinger, introducing our own specific notation. We keep everything as elementary as possible, avoiding sophistry such as the interaction picture, second quantization, Matsubara Green's functions, etc. These are all valuable tools for studying advanced quantum mechanics, but are unnecessary for the basic logic.

3.1 One electron

We start off with the simplest possible case, one electron in one dimension. Recall, from basic quantum mechanics, the Rayleigh-Ritz variational principle:

$$E = \min_{\phi} \langle \phi | \hat{H} | \phi \rangle, \quad \int_{-\infty}^{\infty} dx |\phi(x)|^2 = 1. \quad (3.1)$$

We will use this basic, extremely powerful principle throughout this book. This principle says that we can use *any* normalized wavefunction to calculate the expectation value of the energy for our problem, and we are guaranteed to get an energy above the true ground-state energy. For example, we can use the same wavefunction for *every* 1-d one-electron problem, and get an upper bound on the ground-state energy.

Having learnt about functionals in Chapter 2, we may write this principle in the following useful *functional* form. For example, the kinetic energy of the particle can be considered as a functional of the wavefunction:

$$T[\phi] = \int_{-\infty}^{\infty} dx \phi^*(x) \left(-\frac{1}{2} \frac{d^2}{dx^2} \right) \phi(x) = \frac{1}{2} \int_{-\infty}^{\infty} dx |\phi'(x)|^2 \quad (3.2)$$

where the second form is gotten by integration by parts, and the prime denotes a spatial derivative. (This second form is much handier for many calculations, as you only need take

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one derivative.) Thus, for any given normalized wavefunction, there is a single number T , which can be calculated from it, via Eq. (3.2). Similarly, the potential energy is a very simple functional:

$$V[\phi] = \int_{-\infty}^{\infty} dx V(x) |\phi(x)|^2. \quad (3.3)$$

The kinetic energy of a given wavefunction is always the same, no matter what the problem we are applying that wavefunction to. The kinetic energy is a *universal* functional, independent of the particular problem, i.e., we apply the same operation on a given trial wavefunction, no matter what our physical problem is. But the potential energy functional differs in each problem; it is not universal. This is analogous to trying to find the minimum over x of $f(x, y) = x^2/2 - xy$. The first term is independent of y , so we could make a list of its value for every x , and then use that same list to find the minimum for any y , without having to evaluate it again for each value of y .

Now our variational principle can be written by writing

$$E = \min_{\phi} \{T[\phi] + V[\phi]\}, \quad \int_{-\infty}^{\infty} dx |\phi(x)|^2 = 1 \quad (3.4)$$

We need simply evaluate the energy of all possible normalized wavefunctions, and choose the lowest one.

Exercise 10 Gaussian trial wavefunction

An interesting potential in one-dimension is just $V(x) = -\delta(x)$, where δ is the Dirac delta function. Using a Gaussian wavefunction, $\phi_G(x) = \pi^{-1/4} \exp(-x^2/2)$, as a trial wavefunction, make an estimate for the energy, and a rigorous statement about the exact energy.

We can improve on our previous answers in two distinct ways. The first method is to include an adjustable parameter, e.g., the length scale, into our trial wavefunction.

Exercise 11 Adjustable trial wavefunction

Repeat Ex. (10) with a trial wavefunction $\phi_G(\alpha x)$ (don't forget to renormalize). Find $\langle T \rangle(\alpha)$ and $\langle V \rangle(\alpha)$ and plot their sum as a function of α . Which value of α is the best, and what is your estimate of the ground-state energy? Compare with previous calculation.

Note that this has led to a non-linear optimization problem in α . Varying exponents in trial wavefunctions leads to difficult optimization problems.

An alternative, simpler approach to improving our trial wavefunction is to make a linear combination with other trial wavefunctions, but not vary the length scale. Thus we write

$$\phi_{trial}(x) = c_0 \phi_0(x) + c_1 \phi_1(x), \quad (3.5)$$

and minimize the expectation value of $\hat{H}$, subject to the constraint that ϕ be normalized. This leads to a set of linear equations

$$||\mathbf{H} - E\mathbf{S}|| = 0, \quad (3.6)$$

where

$$H_{ij} = \int_{-\infty}^{\infty} dx \phi_i^*(x) \hat{H} \phi_j(x) \quad (3.7)$$

is the Hamiltonian matrix, and

$$S_{ij} = \int_{-\infty}^{\infty} dx \phi_i^*(x) \phi_j(x) \quad (3.8)$$

is the overlap matrix. In general, Eq. (3.6) is a generalized eigenvalue equation. Only if the basis of trial wavefunctions is chosen as orthonormal (Eq. 1.10) will $\mathbf{S} = \mathbf{1}$, and the equation be an ordinary eigenvalue equation.

Exercise 12 1-d Hydrogen atom

Use $\phi_E(\alpha x)$, where $\phi_E(x) = \exp(-|x|)$ as a trial wavefunction for the problem in Ex. (10). Find the lowest energy. This is the exact answer. Calculate the errors made in the previous exercises, and comment.

The standard textbook problem of chemical bonding is the formation of molecular orbitals from atomic orbitals in describing the molecular ion H_2^+ .

Exercise 13 1-d H_2^+

For a potential $V(x) = -\delta(x) - \delta(x+a)$, use $\phi_{mol}(x) = c_1\phi_E(x) + c_2\phi_E(x+a)$ as a trial wavefunction, and calculate the bonding and antibonding energies as a function of atomic separation a .

There are only slight complications in the real three-dimensional world. We will consider only spherical 3-d potentials, $v(r)$, where $r = |\mathbf{r}|$. Then the spatial parts of the orbitals are characterized by 3 quantum numbers:

$$\phi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\theta, \varphi), \quad (3.9)$$

where the Y_{lm} 's are spherical harmonics. Inserting (3.9) into the Schrödinger Equation gives the radial equation

$$\left\{ -\frac{1}{2r^2} \frac{d}{dr} r^2 \frac{d}{dr} + \frac{l(l+1)}{2r^2} + v(r) \right\} R_{nl}(r) = \varepsilon_{nl} R_{nl}(r). \quad (3.10)$$

These are written about in almost all textbooks on quantum mechanics, with emphasis on the Coulomb problem, $v(r) = -Z/r$. Less frequently treated is the three-dimensional harmonic oscillator problem, $v(r) = kr^2/2$.

Exercise 14 Three dimensions

Use the trial wavefunctions of an exponential and a Gaussian in r to deduce the ground-state energy and orbital of (a) the hydrogen atom ($Z = 1$), and (b) the harmonic oscillator with $k = 1$.

3.2 Two electrons: antisymmetry and spin

When there is more than one particle in the system, the Hamiltonian and the wavefunction includes one coordinate for each particle, as in Eqn. (1.1) for the H_2 molecule. Furthermore, electrons have two possible spin states, up or down, and so the wavefunction is a function both of spatial coordinates and spin coordinates. A general principle of many-electron quantum mechanics is that the wavefunction must be antisymmetric under interchange of any two sets of coordinates. All this is covered in elementary textbooks. For our purposes, this implies the 2-electron wavefunction satisfies:

$$\Psi(\mathbf{r}_2, \sigma_2, \mathbf{r}_1, \sigma_1) = -\Psi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2). \quad (3.11)$$

The ground-states of our systems will be spin-singlets, meaning the spin-part of their wavefunction will be antisymmetric, while their spatial part is symmetric:

$$\Psi(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2) = \Psi(\mathbf{r}_1, \mathbf{r}_2) \chi^{Singlet}(\sigma_1, \sigma_2), \quad (3.12)$$

where the spatial part is symmetric under exchange of spatial coordinates and the spin part $\chi^{Singlet}(\sigma_1, \sigma_2) = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$ is antisymmetric.

3.3 Hartree-Fock for two electrons

For more than one electron, the operators in the Hamiltonian depend on all the coordinates, but in a simple way. Both the kinetic energy and the external potential are one-body operators, meaning that they are sums of terms which each depend on only one coordinate at a time:

$$\hat{T} = -\frac{1}{2} \left(\frac{d^2}{dx_1^2} + \frac{d^2}{dx_2^2} \right) \quad \hat{V}_{\text{ext}} = v_{\text{ext}}(x_1) + v_{\text{ext}}(x_2) \quad (3.13)$$

The electron-electron repulsion operator is a two-body operator, each term depending on two coordinates simultaneously. Note that it is this term that complicates the problem, by coupling the two coordinates together. The interaction between two electrons in three dimensions is Coulombic, i.e., $1/|\mathbf{r} - \mathbf{r}'|$. This is homogeneous of degree -1 in coordinate scaling. However, $1/|x - x'|$ in one-dimension is an exceedingly strong attraction, and we prefer to use $\delta(x - x')$, which has the same scaling property, but is much weaker and more short-ranged.

We will now consider the problem of one-dimensional He as a prototype for two electron problems in general. The Hamiltonian is then:

$$\hat{H} = -\frac{1}{2} \left(\frac{d^2}{dx_1^2} + \frac{d^2}{dx_2^2} \right) - Z\delta(x_1) - Z\delta(x_2) + \delta(x_1 - x_2). \quad (3.14)$$

To find an *exact* solution to this, we might want to solve the Schrödinger equation with this Hamiltonian, but to find approximate solutions, its much easier to use the variational

principle:

$$E = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle, \quad \int dx_1 dx_2 |\Psi(x_1, x_2)|^2 = 1. \quad (3.15)$$

The most naive approach might be to ignore the electron-electron repulsion altogether. Then the differential equation decouples, and we can write:

$$\Psi(x_1, x_2) = \phi(x_1)\phi(x_2) \quad (\text{ignoring } V_{ee}) \quad (3.16)$$

where both orbitals are the same, and satisfy the one-electron problem. We know from chapter 2 that this yields

$$\phi(x) = \sqrt{Z} \exp(-Zx). \quad (3.17)$$

This decoupling of the coordinates makes it possible to handle very large systems, since we need only solve for one electron at a time. However, we have made a very crude approximation to do this. The contribution of the kinetic energy and the potential energy is then just twice as big as in the single electron system:

$$T_s = 2 \left(Z^2/2 \right) \quad V_{\text{ext}} = 2(-Z^2) \quad V_{ee} = 0 \quad (3.18)$$

and therefore the total energy becomes

$$E = 2\epsilon_0 = -Z^2 \quad (3.19)$$

which gives for He ($Z=2$) $E = -4$. This is in fact *lower* than the true ground-state energy of this problem, because we have failed to evaluate part of the energy in the Hamiltonian.

To improve on our estimate, and restore the variational principle, we should evaluate the expectation value of V_{ee} on our wavefunction:

$$V_{ee} = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dx' |\phi(x)|^2 |\phi(x')|^2 \delta(x - x') = Z^2 \int_{-\infty}^{\infty} dx \exp(-4Z|x|) = \frac{Z}{2}. \quad (3.20)$$

For Helium ($Z=2$), $V_{ee} = +1$ so that the ground state energy becomes $E = -4 + 1 = -3$. Because we evaluated all parts of the Hamiltonian on our trial wavefunction, we know that the true $E \leq -3$.

However, using the variational principle, we see that, with almost no extra work, we can do better still. We chose the length scale of our orbital to be that of the $V_{ee} = 0$ problem, i.e., $\alpha = Z$, the nuclear charge. But we can treat this instead as an adjustable parameter, and ask what value minimizes the energy. Inserting this orbital into the components of the energy, we find:

$$T_s = 2 \left(\alpha^2/2 \right) \quad V_{\text{ext}} = -2Z\alpha \quad V_{ee} = \alpha/2 \quad (3.21)$$

so that the total energy, as a function of α , is

$$E(\alpha) = \alpha^2 - 2\alpha(Z - 1/4). \quad (3.22)$$

Minimizing this, we find $\alpha_{min} = Z - 1/4$ and thus

$$E_{min} = -\alpha_{min}^2 = -(Z - 1/4)^2 = -\left(\frac{7}{4}\right)^2 = -3.0625. \quad (3.23)$$

We have lowered the energy by 1/16 of a Hartree, which may not seem like much, but is about 1.7 eV or 40 kcal/mol. Chemical accuracy requires errors of about 1 or 2 kcal/mol.

The best solution to this problem is to find the *orbital* which produces the lowest energy. We could do this by including many variational parameters in a trial orbital, and minimize the energy with respect to each of them, giving up when addition of further parameters has negligible effect. A systematic approach to this would be to consider an infinite set of functions, usually of increasing kinetic energy, and to include more and more of them. However, having learned some functional calculus, we can provide a more direct scheme. The energy, as a functional of the orbital, is:

$$E[\phi] = 2T_s[\phi] + 2V_{ext}[\phi] + U[\phi]/2, \quad U[\phi] = 2 \int_{-\infty}^{\infty} dx |\phi(x)|^4 \quad (3.24)$$

where T_s and V_{ext} are the one-electron functionals mentioned in chapter 2, and U is the 1-d equivalent of the Hartree energy (discussed more below). For two electrons in HF, $V_{ee} = U/2$, and we discuss this much more later. If we simply minimize this a functional of the orbital, subject to the restriction that the orbital is normalized, we find:

$$\left\{ -\frac{1}{2} \frac{d^2}{dx^2} - Z\delta(x) + \frac{1}{2}v_H(x) \right\} \phi(x) = \epsilon\phi(x), \quad (3.25)$$

where

$$v_H(x) = \frac{\delta U}{\delta n(x)} = \int_{-\infty}^{\infty} dx' n(x')\delta(x - x') = n(x) \quad (3.26)$$

is the *Hartree* potential. This is also known as the classical or electrostatic potential, as it is the electrostatic potential due to the charge distribution in classical electrostatics (if the electrostatic interaction were a δ -function, for this case). (Compare with Eq. (1.6) of the introduction.) This equation is the Hartree-Fock equation for this problem.

Exercise 15 Hartree-Fock equations for two electrons

Derive the Hartree-Fock equation for two electrons, Eq. (3.25), by minimizing the energy as a functional of the orbital, Eq. (3.24), keeping the orbital normalized, using the techniques of Chapter 2.

There are several important aspects of this equation which require comment. First, note the factor of 2 dividing the Hartree potential in the equation. This is due to *exchange* effects: The Hartree potential is the electrostatic potential generated by the total charge density due to all the electrons. A single electron should only see the potential due to the *other* electron, hence the division by two. Next, note that these are *self-consistent* equations, since the potential depends on the density, which in turn depends on the

orbital, which is the solution of the equation, etc. These can be solved in practice by the method described in the introduction. To get an idea of what the potential looks like, we construct it for our approximate solution above. There $\alpha = 1.75$ for He, so the potential is a delta function with a Hartree potential of $4 \exp(-7|x|)$. This contribution is positive, pushing the electron farther away from the nucleus. We say the other electron is screening the nucleus. The effective nuclear charge is no longer Z , but rather $Z - 1/4$.

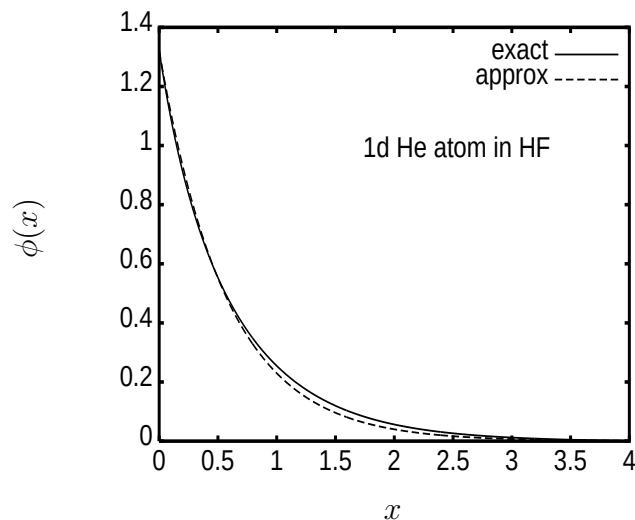


Figure 3.1: Orbitals in HF approximation for 1d He atom, both exact and approximate

It is straightforward to numerically solve the orbital equation Eq. (3.25) on a grid, essentially exactly. But there is an underlying analytic solution in this case, which yields the orbital energy $\epsilon = -(Z - 1/2)^2/2$ ($= -1.125$ for He). But note that this does not mean $E = -(Z - 1/2)^2$. The energy of the effective non-interacting system is *not* the energy of the original interacting system. In this case, from the derivation, we see $E = 2\epsilon - U/2$ (since $\epsilon = T_s + V_{\text{ext}} + U/2$). We find $U/2 = Z/2 - 1/6$, yielding $E = -Z^2 + Z/2 - 1/12$ as the exact HF energy, slightly lower than our simple estimate. In Fig. 3.1, we plot both the exact orbital and the scaled atomic orbital, showing there is very little difference; but this slight difference is enough to reduce the energy by $1/48$, or 0.6 eV or 13 kcal/mol.

Exercise 16 He in 3-d

Repeat the approximate HF calculation for He in three dimensions. What is the orbital energy, the effective nuclear charge, and the total physical energy? Make a rigorous statement about both the exact HF energy and the true ground-state energy. Plot the effective potential (external plus half Hartree) using your approximate solution. (For help, this calculation is done in many basic quantum books).

atom	E^{HF}	E	E_c
He	-2.862	-2.904	-0.042
Be	-14.571	-14.667	-0.096
Ne	-128.555	-128.938	-0.383

Table 3.1: Total energies in HF and exactly for three noble gas atoms.

3.4 Correlation

The approximate solution of the Hartree-Fock equations is not exact, because the true wavefunction is *not* a product of two orbitals, but is rather a complicated function of both variables simultaneously. The true wavefunction satisfies the exact Schrödinger equation, and also minimizes the ground-state energy functional for the given external potential. In traditional quantum chemistry, the correlation energy is defined as the difference between the Hartree-Fock energy and the exact ground-state energy, i.e.,

$$E_c^{\text{trad}} = E - E^{\text{HF}}. \quad (3.27)$$

Table 3.4 lists a few correlation energies for atoms. We see that correlation energies are a very small (but utterly vital) fraction of the total energy of systems. They are usually about 20-40 mH/electron, a result we will derive later. But we strive for chemical accuracy in our approximate solutions, i.e., errors of less than 2 mH per bond. Another important point to note is that in fact, we often do not need *total* energies to this level of accuracy, but rather only energy *differences*, e.g., between a molecule and its separated constituent atoms, in which the correlation contribution might be a much larger fraction, and in which compensating errors might occur in the separate calculation of the molecule and the atoms. An example of this is the *core* electrons, those electrons in closed subshells with energies below the valence electrons, which are often relatively unchanged in a chemical reaction. A large energy error in their contribution is irrelevant, as it cancels out of energy differences.

Exercise 17 Correlation energy

Show that the correlation energy is never positive. When is it zero?

Quantum chemistry has developed many interesting ways in which to calculate the correlation energy. These can mostly be divided into two major types: perturbation theory, and wavefunction calculations. The first is usually in the form of Moller-Plesset perturbation theory, which treats the Hartree-Fock solution as the starting point, and performs perturbation theory in the Coulomb interaction. These calculations are non-variational, and may produce energies below the ground-state energy. Perhaps the most common type of wavefunction calculation is configuration interaction (CI). A trial wavefunction is formed as a linear combination of products of HF orbitals, including excited orbitals, and the energy minimized. In electronic structure calculations of weakly-correlated solids,

most often density functional methods are used. Green's function methods are often applied to strongly-correlated systems.

An interesting paradox to note in chemistry is that most modern chemists think of reactivity in terms of frontier orbitals, i.e., the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied), and their energetic separation, as in Fig. 1.3. In the wavefunction approach, these are entirely constructs of the HF approximation, which makes errors of typically 0.2 Hartrees in binding energies. Thus, although this approximation obviously contains basic chemical information, needed for insight into chemical reactivity, the resulting thermochemistry is pretty bad. On the other hand, to obtain better energetics, one adds many more terms to the approximate wavefunction, losing the orbital description completely. We will see later how DFT resolves this paradox, by showing how an orbital calculation can in principle yield the exact energetics.

3.5 *N* electrons

At this point, we define carefully our notation for electronic systems with N electrons. First, we note that the wavefunction for N electrons is a function of $3N$ spatial coordinates and N spin coordinates. Writing $x_i = (\mathbf{r}_i, \sigma_i)$ to incorporate both, we normalize our wavefunction by:

$$\int dx_1 \dots \int dx_N |\Psi(x_1, \dots, x_N)|^2 = 1, \quad (3.28)$$

where $\int dx$ denotes the integral over all space and sum over both spins. Note that the antisymmetry principle implies

$$\Psi(x_1, \dots, x_j, \dots, x_i, \dots) = -\Psi(x_1, \dots, x_i, \dots, x_j, \dots). \quad (3.29)$$

The electronic density is defined by

$$n(\mathbf{r}) = N \sum_{\sigma} \int dx_2 \dots \int dx_N |\Psi(\mathbf{r}, \sigma, x_2, \dots, x_N)|^2, \quad (3.30)$$

and retains the interpretation that $n(\mathbf{r})d^3r$ is the probability density for finding any electron in a region d^3r around $\mathbf{r}$. The density is normalized to the number of electrons

$$\int d^3r n(\mathbf{r}) = N. \quad (3.31)$$

Our favorite operators become sums over one- and two-particle operators:

$$\hat{T} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2, \quad (3.32)$$

$$\hat{V}_{\text{ext}} = \sum_{i=1}^N v_{\text{ext}}(\mathbf{r}_i), \quad (3.33)$$

and

$$\hat{V}_{ee} = \frac{1}{2} \sum_{i \neq j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (3.34)$$

Note that the factor of 2 in the electron-electron repulsion is due to the sum running over all pairs, e.g., including (1,2) and (2,1). The Schrödinger equation is then

$$(\hat{T} + \hat{V}_{ee} + \hat{V}_{ext}) \Psi(x_1, \dots, x_N) = E \Psi(x_1, \dots, x_N). \quad (3.35)$$

The ground-state energy can be extracted from the variational principle:

$$E = \min_{\Psi} \langle \Psi | \hat{T} + \hat{V}_{ee} + \hat{V}_{ext} | \Psi \rangle, \quad (3.36)$$

once the minimization is performed over all normalized antisymmetric wavefunctions.

In the special case of non-interacting particles, we denote the wavefunction by Φ instead of Ψ , and this will usually be a single Slater determinant of occupied orbitals, i.e.,

$$\Phi(x_1, \dots, x_N) = \begin{vmatrix} \phi_1(x_1) & \cdots & \phi_N(x_1) \\ \vdots & & \vdots \\ \phi_1(x_N) & \cdots & \phi_N(x_N) \end{vmatrix} \quad (3.37)$$

For systems with equal numbers of up and down particles in a spin-independent external potential, the full orbitals can be written as a product, $\phi_i(x) = \phi_i(\mathbf{r})|\sigma\rangle$, and each spatial orbital appears twice. Thus, the Hartree-Fock energy is

$$E = \min_{\Phi} \langle \Phi | \hat{T} + \hat{V}_{ee} + \hat{V}_{ext} | \Phi \rangle, \quad (3.38)$$

and the Hartree-Fock equations are...

The Coulomb interaction for a single Slater determinant yields, due to the antisymmetric nature of the determinant, two contributions:

$$\langle \Psi | \hat{V}_{ee} | \Psi \rangle = U[\Psi] + E_x[\Psi]. \quad (3.39)$$

The first of these is called the direct or Coulomb or electrostatic or classical contribution, given in Eq. 2.10, with the density being the sum of the squares of the occupied orbitals. This is the electrostatic energy of the charge density in electromagnetic theory, ignoring its quantum origin. The second is the Fock or exchange integral, being

$$E_x[\phi_i] = -\frac{1}{2} \sum_{\sigma} \sum_{\substack{i,j \\ occ}} \int d^3r \int d^3r' \frac{\phi_{i\sigma}^*(\mathbf{r}) \phi_{j\sigma}^*(\mathbf{r}') \phi_{i\sigma}(\mathbf{r}') \phi_{j\sigma}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \quad (3.40)$$

for a determinant of doubly-occupied orbitals. This is a purely Pauli-exclusion principle effect.

Exercise 18 Exchange energies for one and two electrons

Argue that, for one electron, $E_x = -U$, and show that, for two electrons in a singlet, $E_x = -U/2$.

3.6 Electronic densities

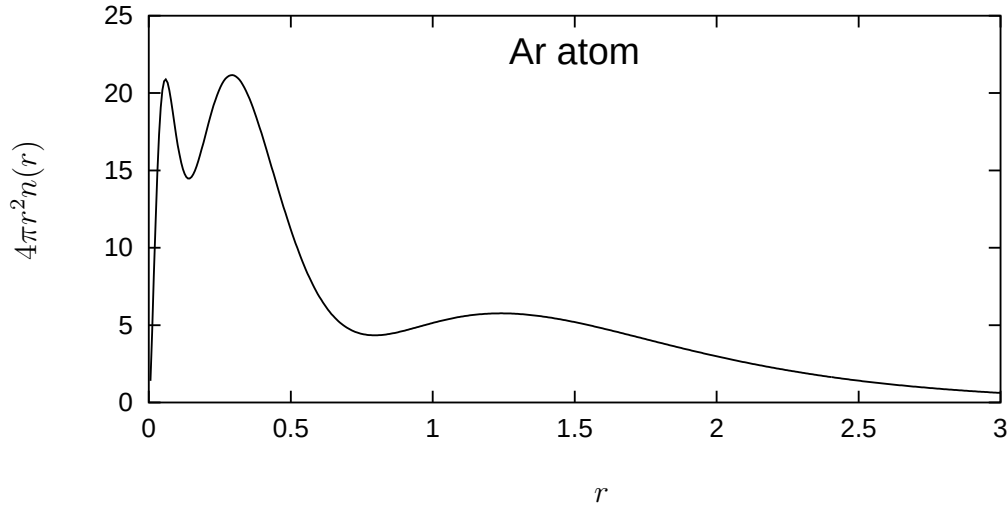


Figure 3.2: Radial density in Ar atom.

All atomic densities, when plotted as function of r with the nucleus at the origin, have been found to decay monotonically, although that's never been generally proven. Close to a nucleus, the external potential dominates in the Schrödinger equation, and causes a cusp in the density, whose size is proportional to the nuclear charge:

$$\left. \frac{dn}{dr} \right|_{r=0} = -2Z n(0) \quad (3.41)$$

for a nucleus of charge Z at the origin. This is Kato's cusp condition, and we already saw examples of this in earlier exercises. It is also true in our one-dimensional examples with delta-function external potentials.

Typically, spherical densities are plotted multiplied by the phase-space factor $4\pi r^2$. This means the area under the curve is precisely N . Furthermore, the different electronic shells are easily visible. We take the Ar atom as an example. In Fig. 3.2, we plot its radial density. This integrates to 18 electrons. We find that the integral up to $r = 0.13$ contains 2 electrons, up to 0.25 contains 4, 0.722 contains 10, and 1.13 contains 12. These correspond to the 2 1s electrons, 2 2s electrons, 6 2p electrons, and 2 3s electrons, respectively. Note that the peaks and dips in the radial density roughly correspond to these shells.

The decay at large distances is far more interesting. When one coordinate in a wavefunction is taken to large distances from the nuclei, the N -electron ground-state wavefunction collapses to the product of the square-root of the density times the $(N - 1)$ -electron wavefunction. This means the square-root of the density satisfies a Schrödinger-like equation, whose eigenvalue is the difference in energies between the two systems:

$$\sqrt{n(r)} = A r^\beta \exp(-\alpha r) \quad (r \rightarrow \infty) \quad (3.42)$$

where $\alpha = \sqrt{2I}$, and

$$I = E(N - 1) - E(N) \quad (3.43)$$

is first ionization potential. In fact, the power can also be deduced, $\beta = (Z - N + 1)/\alpha - 1$, and A is some constant. Thus, a useful and sensitive function of the density to plot for spherical systems is

$$\kappa(r) = (1/2) \frac{d \log(n(r))}{dr}, \quad (3.44)$$

since $\kappa(0) = -Z$, while $\kappa(r) \rightarrow -\alpha$, as $r \rightarrow \infty$. The ground-state density can always be reconstructed from

$$n(r) = C \exp\left(\int_r^\infty dr' 2\kappa(r')\right) \quad (3.45)$$

where the constant is determined by normalization.

In a one-dimensional world with delta function interactions, these conditions remain true, except for the details of the power law in front of the exponential in Eq. (3.42). In particular, we have already seen the cusp in the orbital for 1-d hydrogenic atoms. We may see dramatic evidence for these conditions in our HF solution of the 1-d He atom, by plotting $\kappa(x)$ on the left of Fig. 3.3. Near the nucleus, the exact cusp condition is satisfied, so that κ equals -2, but at large distances, it tends to a smaller constant, determined by the ionization potential. We can also clearly see the difference between the approximate and exact HF solutions here, which was not so visible in the last figure. On the right, we have also plotted $\kappa(r)$ for real He, and see that the effect of correlation on the density is extremely small: The HF and exact densities are very close.

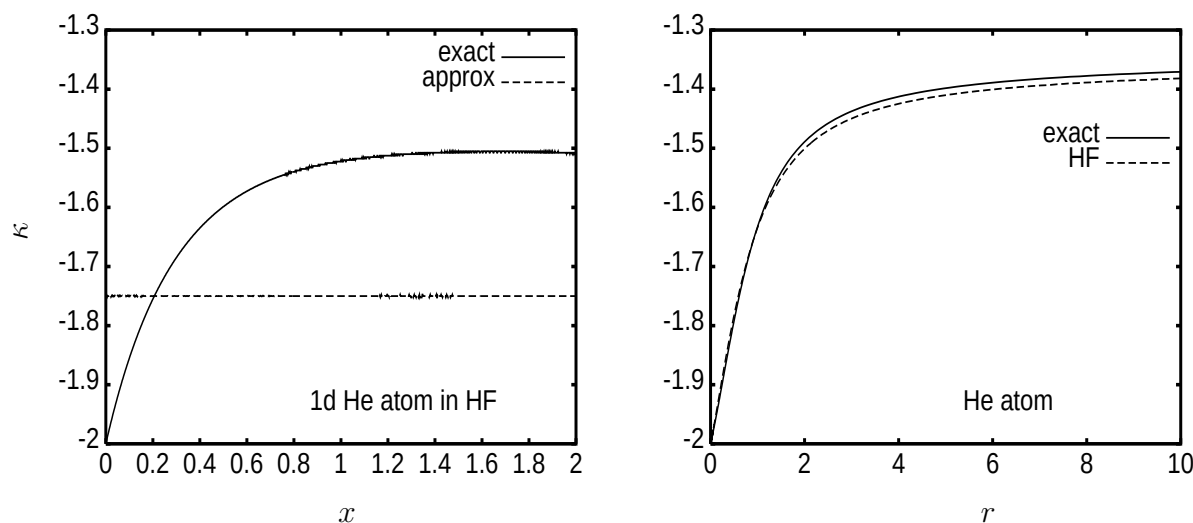


Figure 3.3: κ in (a) 1d He atom in HF approximation, both exact and approximate; (b) in real He, in HF and exactly

In fact, the density of all spherical atoms have always been found to be monotonically decreasing for all r , but no-one has yet proven this fact.

3.7 Questions about wavefunction quantum mechanics

1. *Suggest a good trial wavefunction for a potential that consists of a negative delta function in the middle of a box of width L .*
2. *What is the effect of having nuclear charge $Z \neq 1$ for the 1-d H-atom?*
3. *What is the exact kinetic energy density functional for one electron in one-dimension?*
4. *Is the HF estimate of the ionization potential for 1-d He an overestimate or underestimate?*
5. *Consider the approximate HF calculation given in section 3.3. Comment on what it does right, and what it does wrong. Suggest a simple improvement.*
6. *Which is bigger, the kinetic energy of the true wavefunction or that of the HF wavefunction for 1d He? Hooke's atom?*

Answers

1. The simplest guess is just that of the particle in the box, $\sqrt{2/L} \cos(\pi x/L)$. Its energy is obviously $\pi^2/2L^2 - 2Z/L$, where Z is the strength of the delta function. Much better (in fact, exact) is to take linear combinations of the delta-function solutions, $\exp(-\alpha|x|)$ and $\exp(\alpha|x|)$ vanishing at the edges.
2. It alters the length scale of the wavefunction without changing its normalization, i.e., $\sqrt{Z} \exp(-Z|x|)$. We see shortly how this can be a handy trick.
3. It is the von Weisacker functional,

$$T_s^{\text{vw}} = \frac{1}{2} \int_{-\infty}^{\infty} dx |\phi'(x)|^2 = \frac{1}{2} \int_{-\infty}^{\infty} dx |n'(x)|^2 / (8n(x)). \quad (3.46)$$

4. The ionization potential is $I = E_1 - E_2$ for a two-electron system, where E_N is the energy with N electrons. Since $E^{\text{HF}} \geq E$, with equality for one electron, $I^{\text{HF}} < I$.
5. The HF calculation correctly writes the wavefunction as a spatially symmetric singlet, but incorrectly approximates that as a product of separate functions of x_1 and x_2 (orbitals). It correctly satisfies the cusp condition at the nucleus, and changes decay at large distance, unlike the scaled orbital solution. But its energy is not low enough.
6. The virial theorem applies to this problem (see section X), and, since all potentials are homogeneous of order -1 , $E = -T = -V/2$, where V includes both the external and the electron-electron interaction. Since $E^{\text{HF}} > E$, then $T^{\text{HF}} < T$. For Hooke's atom, the situation is more complicated, since there are two different powers in the potentials.

Chapter 4

Modern density functional theory

¹ This chapter deals with the foundation of modern density functional theory as an *exact* approach (in principle) to systems of interacting particles. In our case, electrons, i.e., fermions interacting via the Coulomb repulsion.

4.1 DFT for one electron in one dimension

4.2 Hohenberg-Kohn theorems

It is self-evident that the external potential in principle determines all the properties of the system: this is the normal approach to quantum mechanical problems, by solving the Schrödinger equation for the eigenstates of the system.

The first Hohenberg-Kohn theorem demonstrates that the density may be used in place of the potential as the basic function uniquely characterizing the system. It may be stated as: the ground-state density $n(\mathbf{r})$ uniquely determines the potential, up to an arbitrary constant.

In the original Hohenberg-Kohn paper, this theorem is proven for densities with non-degenerate ground states. The proof is elementary, and by contradiction. Suppose there existed two potentials differing by more than a constant, yielding the same density. These would have two different ground-state wavefunctions, Ψ_1 and Ψ_2 . Consider Ψ_2 as a trial wavefunction for potential $v_{\text{ext},1}(\mathbf{r})$. Then, by the variational principle,

$$\langle \Psi_2 | \hat{T} + \hat{V}_{\text{ee}} + \hat{V}_{\text{ext},1} | \Psi_2 \rangle \geq \langle \Psi_1 | \hat{T} + \hat{V}_{\text{ee}} + \hat{V}_{\text{ext},1} | \Psi_1 \rangle. \quad (4.1)$$

But since both wavefunctions have the same density, this implies

$$\langle \Psi_2 | \hat{T} + \hat{V}_{\text{ee}} | \Psi_2 \rangle \geq \langle \Psi_1 | \hat{T} + \hat{V}_{\text{ee}} | \Psi_1 \rangle. \quad (4.2)$$

But we can always swap which wavefunction we call 1 and which we call 2, which reverses this inequality, leading to a contradiction, unless the total energies of the two

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wavefunctions are the same, which implies they are the same wavefunction by the variational principle and the assumption of non-degeneracy. Then, simple inversion of the Schrödinger equation, just as we have done several times for the one-electron case, yields

$$\sum_{i=1}^N v_{\text{ext}}(\mathbf{r}_i) = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 \Psi / \Psi + \frac{1}{2} \sum_{j \neq i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (4.3)$$

This determines the potential up to a constant.

Exercise 19 Finding the potential from the density

For the smoothed exponential, $\phi(x) = C(1 + |x|) \exp(-|x|)$, find the potential for which this is an eigenstate, and plot it. Is it the ground state of this potential?

An elegant constructive proof was found later by Levy, which automatically includes degenerate states. It is an example of the constrained search formalism. Consider all wavefunctions Ψ which yield a certain density $n(\mathbf{r})$. Define the functional

$$F[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{V}_{\text{ee}} | \Psi \rangle \quad (4.4)$$

where the search is over all antisymmetric wavefunctions yielding $n(\mathbf{r})$. Then, for any $n(\mathbf{r})$, *any* wavefunction minimizing $\hat{T} + \hat{V}_{\text{ee}}$ is a ground-state wavefunction, since the ground-state energy is simply

$$E = \min_n \left(F[n] + \int d^3r v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \right), \quad (4.5)$$

from the variational principle, where the search is over all normalized positive densities. Any such wavefunction can then be fed into Eq. (4.3) to construct the unique corresponding potential. We denote the minimizing wavefunction in Eq. (4.4) by $\Psi[n]$. This gives us a verbal definition of the ground-state wavefunction. *The exact ground-state wavefunction of density $n(\mathbf{r})$ is that wavefunction that yields $n(\mathbf{r})$ and has minimizes $T + V_{\text{ee}}$.* We may also define the exact kinetic energy functional as

$$T[n] = \langle \Psi[n] | \hat{T} | \Psi[n] \rangle, \quad (4.6)$$

and the exact electron-electron repulsion functional as

$$V_{\text{ee}}[n] = \langle \Psi[n] | \hat{V}_{\text{ee}} | \Psi[n] \rangle. \quad (4.7)$$

The second Hohenberg-Kohn theorem states that the functional $F[n]$ is *universal*, i.e., it is the same functional for all electronic structure problems. This is evident from Eq. (4.4), which contains no mention of the external potential. To understand the content of this statement, consider some of our previous problems. Recall our orbital treatment of one-electron problems. The kinetic energy functional, $T[\phi] = \frac{1}{2} \int dx |\phi'(x)|^2$, is the *same* functional for all one-electron problems. When we evaluate the kinetic energy for a given trial orbital, it is the same for that orbital, regardless of the particular problem

being solved. Similarly, when we treated the two electron case within the Hartree-Fock approximation, we approximated

$$F[n] \approx F^{\text{HF}}[n] = \frac{1}{8} \int d^3r \frac{|\nabla n|^2}{n} + \frac{1}{4} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (4.8)$$

Then minimization of the energy functional in Eq. (4.5) with $F^{\text{HF}}[n]$ yields precisely the Hartree-Fock equations for the two-electron problem. The important point is that this single formula for $F^{\text{HF}}[n]$ is all that is needed for *any* two-electron Hartree-Fock problem. The second Hohenberg-Kohn theorem states that there is a single $F[n]$ which is *exact* for *all* electronic problems.

Exercise 20 Errors in Hartree-Fock functional

Comment, as fully as you can, on the errors in $F^{\text{HF}}[n]$ relative to the exact $F[n]$ for two electrons.

The last part of the Hohenberg-Kohn theorem is the Euler-Lagrange equation for the energy. We wish to minimize $E[n]$ for a given $v_{\text{ext}}(\mathbf{r})$ keeping the particle number fixed. We therefore minimize $E[n] - \mu N$, as in chapter 2, and find the Euler-Lagrange equation:

$$\frac{\delta F}{\delta n(\mathbf{r})} + v_{\text{ext}}(\mathbf{r}) = \mu. \quad (4.9)$$

We can identify the constant μ as the chemical potential of the system, since $\mu = \partial E / \partial N$. The exact density is such that it makes the functional derivative of F exactly equal to the negative of the external potential (up to a constant). Note that it would be marvellous if we could find an adequate approximation to F for our purposes, so that we could solve Eq. (4.9) directly. It would yield a single integrodifferential equation to be solved, probably by a self-consistent procedure, for the density, which could then be normalized and inserted back into the functional $E[n]$, to recover the ground-state energy. In the next section, we will examine the original crude attempt to do this (Thomas-Fermi theory), and find that, although the overall trends are sound, the accuracy is insufficient for modern chemistry and materials science. Note also that insertion of $F^{\text{HF}}[n]$ will yield an equation for the density equivalent to the orbital HF equation.

An important formal question is that of v -representability. The original HK theorem was proven only for densities that were ground-state densities of some interacting electronic problem. The constrained search formulation extended this to any densities extracted from a single wavefunction, and this domain has been further extended to densities which result from ensembles of wavefunctions. The interested reader is referred to Dreizler and Gross for a thorough discussion.

4.3 Thomas-Fermi theory: A blast from the past

In this section, we briefly discuss the first density functional theory (1927), its successes, and its limitations. Note that it predates Hartree-Fock by three years.

In the Thomas-Fermi theory, $F[n]$ is approximated by the local approximation for the (non-interacting) kinetic energy of a uniform gas, plus the Hartree energy

$$F^{\text{TF}}[n] = A_s \int d^3r n^{5/3}(\mathbf{r}) + \frac{1}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (4.10)$$

Several points need to be clarified. First, these expressions were developed for a spin-unpolarized system, i.e., one with equal numbers of up and down spin electrons, in a spin-independent external potential. Second, in the kinetic energy, we saw in Chapter ?? how the power of n can be deduced by dimensional analysis, while the coefficient is chosen to agree with that of a uniform gas, yielding $A_s = (3/10)(3\pi^2)^{2/3}$. We will derive these numbers in detail in Chapter X. They can also be derived by classical arguments applied to the electronic fluid.

Insertion of this approximate F into the Euler-Lagrange equation yields the Thomas-Fermi equation:

$$\frac{5}{3}A_s n^{2/3}(\mathbf{r}) + \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{ext}}(\mathbf{r}) = \mu \quad (4.11)$$

We will focus on its solution for spherical atoms, which can easily be achieved numerically with a simple ordinary differential equation solver. We can see immediately some problems. As $r \rightarrow 0$, because of the singular Coulomb external potential, the density is singular, $n \rightarrow 1/r^{3/2}$ (although still integrable, because of the phase-space factor $4\pi r^2$). Again, as $r \rightarrow \infty$, the density decays with a power law (or worse), not exponentially. But overall, the trends will be approximately right. To see this, do the following exercise:

Exercise 21 Atomic calculations

Assume the density of an atom is exponentially decaying, i.e., $n(r) = \exp(-\alpha r)$, where α is to be determined.

1. Normalize your density for N electrons.
2. Approximate the energy of your atom by:

$$E = T_s + V_{\text{ext}} + U + E_x^{\text{LDA}}, \quad (4.12)$$

where the non-interacting kinetic energy is

$$T_s^{\text{TF}}[n] = A_s \int d^3r n^{5/3}(\mathbf{r}), \quad A_s = 2.871, \quad (4.13)$$

the Hartree energy is

$$U = \frac{1}{2} \int d^3r \int d^3r' n(\mathbf{r}) n(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'|, \quad (4.14)$$

the external potential is

$$V_{\text{ext}} = \int d^3r n(\mathbf{r})(-Z/r), \quad (4.15)$$

and

$$E_x^{\text{LDA}} = A_x \int d^3r n^{4/3}(\mathbf{r}), \quad A_x = -(3/4)(3/\pi)^{1/3} = -0.738. \quad (4.16)$$

By doing the integrals for your trial density, find an expression for $E(\alpha)$. You may find it useful that for the hydrogen atom, $U = 0.375$.

3. Find a formula for the optimum value of α as a function of N and Z , and for the corresponding energy.
4. The total ground-state energies of the He, Ne, Ar, Kr, Xe, and U atoms are -2.9, -129, -530, -2700, -7200, and -27,000, respectively. Compare with your results.
5. Calculate the radius of your atoms. What chemical ‘radius’ does it approximate, and how well does it do?
6. Calculate the ionization potentials for the Noble gas atoms and compare with experiment. Comment
7. Repeat above across the second row.
8. Repeat your calculations with the LDA exchange turned off. Comment on its effect on the density and radius and energy.
9. A more accurate estimate of the kinetic energy is given by adding 1/9 the von Weisacker energy, i.e.,

$$T_s = T_s^{\text{TF}} + T^{\text{VW}}/9 \quad (4.17)$$

where

$$T_s^{\text{VW}}[n] = \int d^3r |\nabla n|^2/(8n) \quad (4.18)$$

Add this in, repeat all previous questions, and comment on changes.

Exercise 22 Variational Thomas-Fermi

A neat way to approximate the Thomas-Fermi density is

$$n(r) = C(R/r)^{3/2} \exp(-r/R). \quad (4.19)$$

Note that R is simply $1/\gamma$, the scale factor.

1. Normalize to N electrons.
2. Show $T = \alpha N^{5/3}/R^2$, $U = 2\beta N^2/R$, and $V_{\text{ext}} = -2NZ/R$, where $\alpha = 0.892$ and $\beta = 0.17$.
3. Minimize the total energy w.r.t. to R , to find expressions for R_o and E_o .
4. The total ground-state energies of the He, Ne, Ar, Kr, Xe, and U atoms are -2.9, -129, -530, -2700, -7200, and -27,000, respectively. Calculate these values in TF, and the values of R_o , and comment on the trends. What chemical radius does R_o estimate?
5. For Ar^{16+} , Ar^{14+} , and Ar^{8+} , the energy is -320, -380, and -510. Plot both the exact and TF curves of E vs. N for Ar. Comment.
6. An accurate radial density for the Xe atom is given in Fig. 4.1. Compare with your approximate TF density, and comment.

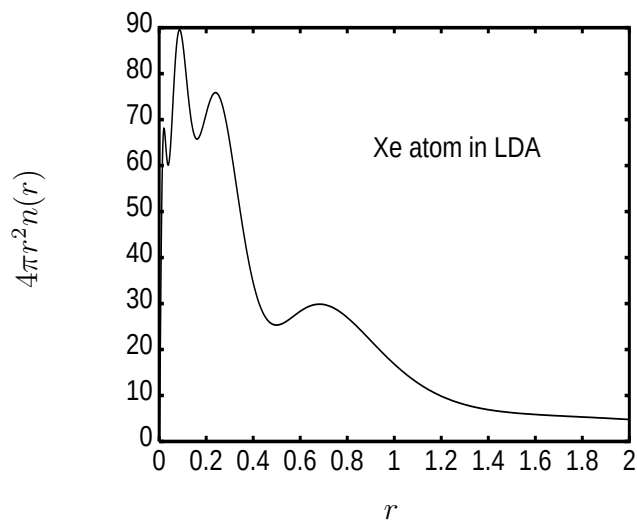


Figure 4.1: Radial density in the Xe atom, calculated using LDA.

Lastly, Teller showed that molecules do not bind in TF theory, because the errors in TF are far larger than the relatively small binding energies of molecules.

4.4 Kohn-Sham equations

The major error in the Thomas-Fermi approach comes from approximating the kinetic energy as a density functional. We saw in chapter one that local approximations to the kinetic energy are typically good to within 10%. However, since for Coulombic systems, the kinetic energy equals the absolute value of the total energy, errors of 10% are huge. Even if we could reduce errors to 1%, they would still be too large. A major breakthrough in this area is provided by the Kohn-Sham construction of non-interacting electrons with the same density as the physical system, because solution of the Kohn-Sham equations produces the exact non-interacting kinetic energy, which includes almost all the true kinetic energy.

We now have the theoretical tools to immediately write down these KS equations. Recall from the introduction, that the KS system is simply a fictitious system of non-interacting electrons, chosen to have the same density as the physical system. Then its orbitals are given by Eq. (1.5), i.e.,

$$\left\{ -\frac{1}{2}\nabla^2 + v_s(\mathbf{r}) \right\} \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \quad (4.20)$$

and yield

$$n(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2. \quad (4.21)$$

The subscript s denotes single-electron equations. But the Euler equation that is equivalent to these equations is

$$\frac{\delta T_s}{\delta n(\mathbf{r})} + v_s(\mathbf{r}) = \mu, \quad (4.22)$$

where

$$T_s[n] = \min_{\Phi \rightarrow n} \langle \Phi | \hat{T} | \Phi \rangle, \quad (4.23)$$

is the kinetic energy of non-interacting electrons. We have implicitly assumed that the Kohn-Sham wavefunction is a single Slater determinant, which is true most of the time. We denote the minimizing wavefunction in Eq. (4.23) by $\Phi[n]$. This gives us a verbal definition of the Kohn-Sham wavefunction. *The Kohn-Sham wavefunction of density $n(\mathbf{r})$ is that wavefunction that yields $n(\mathbf{r})$ and has least kinetic energy.* Obviously $T_s[n] = \langle \Phi[n] | \hat{T} | \Phi[n] \rangle$, which differs from $T[n]$.

Exercise 23 Kinetic energies

Show that $T[n] \geq T_s[n]$. What is the relation between $T^{\text{HF}}[n]$ and $T_s[n]$? Is there a simple relation between $T[n]$ and $T^{\text{HF}}[n]$?

Now, write the ground-state functional of an interacting system in terms of the non-interacting kinetic energy:

$$F[n] = T_s[n] + U[n] + E_{\text{xc}}[n]. \quad (4.24)$$

We have explicitly included the Hartree energy, as we know this will be a large part of the remainder, and we know it explicitly as a density functional. The rest is called the exchange-correlation energy. Inserting $F[n]$ into Eq. (4.9) and comparing with Eq. (4.22), we find

$$v_s(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{xc}}[n](\mathbf{r}) \quad v_{\text{xc}}(\mathbf{r}) = \delta E_{\text{xc}} / \delta n(\mathbf{r}) \quad (4.25)$$

This is the first and most important relationship of exact density functional theory: from the functional dependence of $F[n]$, we can extract the potential felt by non-interacting electrons of the same density.

We note several important points:

- The Kohn-Sham equations are exact, and yield the exact density. For every physical system, the Kohn-Sham alter ego is well-defined and unique. There is nothing approximate about this.
- The Kohn-Sham equations are a set of single-particle equations, and so are much easier to solve than the coupled Schrödinger equation, especially for large numbers of electrons. However, in return, the unknown exchange-correlation energy must be approximated. (We do not know this functional exactly, or else we would have solved all Coulomb-interacting electronic problems exactly.)
- While the KS potential is unique by the Hohenberg-Kohn theorem (applied to non-interacting electrons), there are known examples where such a potential cannot be found. In common practice, this has never been a problem.
- The great advantage of the KS equations over Thomas-Fermi theory is that almost all the kinetic energy (T_s) is treated exactly.
- The KS orbitals supercede the HF orbitals, in providing an exact molecular orbital theory. With exact KS theory, we see now how an orbital calculation can provide exact energetics. The HF orbitals are better thought of as approximations to exact KS orbitals. So the standard figure, Fig. 1.3, and other orbital pictures, are much more usefully interpreted as pictures of KS atomic and molecular orbitals.
- Note that pictures like that of Fig. 1.2 tell us nothing about the functional dependence of $v_s(\mathbf{r})$. That KS potential was found simply by inverting the non-interacting Schrödinger equation for a single orbital. This gives us the exact KS potential for this system, but tells us nothing about how that potential would change with the density.
- By subtracting T_s and U from F , what's left (exchange and correlation) will turn out to be very amenable to local type approximations.

4.5 DFT exchange

In density functional theory, we define the exchange energy as

$$E_x[n] = \langle \Phi[n] | \hat{V}_{ee} | \Phi[n] \rangle - U[n], \quad (4.26)$$

i.e., the electron-electron repulsion, evaluated on the Kohn-Sham wavefunction, yields a direct contribution (the Hartree piece) and an exchange contribution. In most cases, the Kohn-Sham wavefunction is simply a single Slater determinant of orbitals, so that E_x is given by the Fock integral, Eq. (3.40) of the KS orbitals. These differ slightly from the Hartree-Fock orbitals, in that they are the orbitals that yield a given density, but that are eigenstates of a single potential (not orbital-dependent). Note that Eq. (3.40) does *not* give us the exchange energy as an explicit functional of the density, but only as a functional of the orbitals. The total energy in a Hartree-Fock calculation is extremely close to $T_s + U + V_{\text{ext}} + E_x$.

Exercise 24 Old versus new

Prove $E^{\text{HF}} \leq T_s + U + V_{\text{ext}} + E_x$ for any problem.

Exercise 25 Exchange energies

Calculate the exchange energy for the hydrogen atom and for the three-dimensional harmonic oscillator. If I construct a spin singlet, with both electrons in an exponential orbital, what is the exchange energy then?

4.6 DFT correlation

In density functional theory, we then define the correlation energy as the remaining unknown piece of the energy:

$$E_c[n] = F[n] - T_s[n] - U[n] - E_x[n]. \quad (4.27)$$

We will show that it is usually better to approximate exchange-correlation together as a single entity, rather than exchange and correlation separately. Inserting the definition of F above, we find that the correlation energy consists of two separate contributions:

$$E_c[n] = T_c[n] + U_c[n] \quad (4.28)$$

where T_c is the kinetic contribution to the correlation energy,

$$T_c[n] = T[n] - T_s[n] \quad (4.29)$$

(or the correlation contribution to kinetic energy), and U_c is the potential contribution to the correlation energy,

$$U_c[n] = V_{ee}[n] - U[n] - E_x[n]. \quad (4.30)$$

For many systems, $T_c \sim -E_c \sim -U_c/2$.

Exercise 26 Correlation energy

Prove $E_C \leq 0$, and say which is bigger: E_C or E_C^{trad} .

4.7 Questions about modern density functional theory

1. How would you go about finding the potential from the wavefunction of a two-electron system? For two electrons, can more than one potential have the same ground-state density?
2. Define the ground-state wavefunction generating density $n(\mathbf{r})$, without mentioning the external potential.
3. Define the ground-state Kohn-Sham wavefunction generating density $n(\mathbf{r})$.
4. Consider two normalized orbitals in one dimension, $\phi_1(x)$ and $\phi_2(x)$, and the density $n = |\phi_1|^2 + |\phi_2|^2$. What is the Kohn-Sham kinetic energy of that density? How does it change when we alter one of the orbitals? Repeat the question for the Kohn-Sham exchange energy.
5. The exchange energy of the orbitals is the same in Hartree-Fock and Kohn-Sham theory. What is the relation between the two for the Hartree-Fock density?
6. Considering the exact relations for the asymptotic decay of the density of Coulombic systems, is there any significance to ϵ_{HOMO} for the KS system? (See section 8.5).

Answers

1. The ground-state wavefunction is that normalized, antisymmetric wavefunction that has density $n(\mathbf{r})$ and minimizes the kinetic plus Coulomb repulsion operators.
2. The Kohn-Sham wavefunction of density $n(\mathbf{r})$ is that normalized, antisymmetric wavefunction that has density $n(\mathbf{r})$ and minimizes the kinetic operator.
3. The Kohn-Sham kinetic energy is *not* $\frac{1}{2} \int dx |\phi_1'|^2 + |\phi_2'|^2$, because these orbitals could have come from anywhere. There is no reason to think they are Kohn-Sham orbitals. They might be, e.g., Hartree-Fock orbitals. The way to get T_s is to construct the density $n(x)$ and then find $v_s(x)$, a local potential that, with two occupied orbitals, yields that density. The kinetic energy of *those* two orbitals is then T_s . Again, if we alter one of the original orbitals, the change in T_s is *not* the kinetic contribution directly due to that orbital. Rather, one must calculate the new density, construct the new Kohn-Sham potential, get the kinetic energy of its orbitals, and that tells you the change.

All the same reasoning applies for $E_x[n]$.

4. See above. One can do a HF calculation, yielding orbitals and density. Then E_x^{HF} is simply the Fock integral of those orbitals. But this is *not* $E_x[n^{\text{HF}}]$, which could only be found by finding the local potential $v_s(\mathbf{r})$ whose orbitals add up to $n^{\text{HF}}(\mathbf{r})$, and evaluating the Fock integral on its orbitals.
5. The additional flexibility of spin-DFT over DFT means that its much easier to make good approximations for spin-polarized systems.
6. Given $v_{s\sigma}(\mathbf{r})$, solve the Kohn-Sham equations for up and down non-interacting electrons in these potentials, and construct the total density. Then ask what single potential all electrons must feel in the Kohn-Sham equations to reproduce that density. Obviously, they coincide when the system is unpolarized, so that $v_{s\sigma}(\mathbf{r}) = v_s(\mathbf{r})$, and when fully polarized, $v_{s\uparrow}(\mathbf{r}) = v_s(\mathbf{r})$, $v_{s\downarrow}(\mathbf{r}) = 0$ or undetermined.
7. No. See further work whead.

Chapter 5

The local density approximation

¹ This chapter deals with the simplest and most successful approximation within density functional theory, namely the local approximation for exchange and correlation.

5.1 Local density approximation (LDA)

The simplest and easiest to implement density functional approximation is a local one, in which the functional is a simple integral over a *function* of the density at each point in space:

$$E_{\text{xc}}^{\text{loc}}[n] = \int d^3r f(n(\mathbf{r})) \quad (5.1)$$

where $f(n)$ is some function of n . To determine this function, we use the same logic as in chapter ?? and ask: For what system can this functional be exact?

5.2 Uniform electron gas

The local approximation is *exact* for the special case of a uniform electronic system, i.e., one in which the electrons sit in an infinite region of space, with a uniform positive external potential, chosen to preserve overall charge neutrality. The kinetic and exchange energies of such a system are easily evaluated, since the Kohn-Sham wavefunctions are simply Slater determinants of plane waves. The correlation energy is extracted from accurate Monte Carlo calculations, combined with known exact limiting values.

For the non-interacting kinetic energy of electrons of a given spin in one-dimension, as was used in the introduction, we can do this derivation. Put N electrons in a infinite box, stretching from 0 to L . They occupy the lowest N eigenstates. Then consider taking N and $L \rightarrow \infty$, keeping $n = N/L$ fixed. As the number gets very large, the density profile

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$n(x) \rightarrow n$ as $x \rightarrow L/2$, the interior of the box. We write

$$n(x) = (2/L) \sum_{j=1}^N \sin^2(k_j x) \quad (5.2)$$

where $k_j = j\pi/L$, $j = 1, 2, \dots$. In the thermodynamic limit ($L \rightarrow \infty$), the spacing between levels gets very small, and the sum can be replaced by an integral. To do this, insert $\Delta j = 1 = \Delta k L/\pi$ inside the sum. Then change the sum over j to an integral over k , with $\Delta k \rightarrow dk$ as $L \rightarrow \infty$, yielding

$$n(x) = 2 \int_0^{k_F} \frac{dk}{\pi} \frac{1}{2} (1 - \cos(2kx)) = \frac{k_F}{\pi} \left(1 - \frac{\sin(2k_F x)}{2k_F x} \right) \quad (5.3)$$

where $k_F = N\pi/L$ is the wavevector of the HOMO, called the Fermi wavevector. This density is plotted for $N = L$ in Fig. 5.1. The density tends to the correct bulk value as

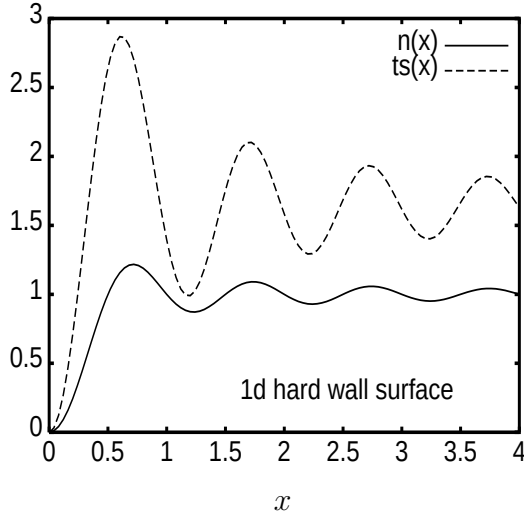


Figure 5.1: Density and kinetic energy density at one-dimensional surface.

$x \rightarrow \infty$ and the oscillating terms die away; it also vanishes as $x \rightarrow 0$, the edge of the box; and the oscillating terms have wavelength π/k_F , and are called Friedel oscillations. Similarly, we find the contribution to the non-interacting kinetic energy at a point to be

$$t_s(x) = (2/L) \sum_{j=1}^N (k_j^2/2) \sin^2(k_j x) = \frac{\pi^2}{6} n^3 (1 - f(2k_F x)) \quad (5.4)$$

where $f(y) = 3(\sin(y)/y + 2 \cos(y)/y^2 - 2 \sin(y)/y^3)$. The bulk value ($x \rightarrow \infty$) provides us with the coefficient in the local approximation to $T_s[n]$, and as $y \rightarrow 0$, $f(y) = 1 - 3y^2/10$.

Exercise 27 Surface energy *The surface energy of a system is the energy required to create a surface. It is found by subtracting from the energy of a system with a surface the energy of an equal number of bulk electrons. Calculate the surface kinetic energy of our same-spin 1-d electrons in a large box, and compare with the local approximation.*

If we repeat the exercise above in three dimensions, we find that it is simpler to use plane-waves with periodic boundary conditions. The states are then ordered energetically by momentum, and the lowest occupied levels form a sphere in momentum-space. Its radius is called the Fermi wavevector, and is given by

$$k_F = (3\pi^2 n)^{1/3}, \quad (5.5)$$

where the different power and coefficient come from the different dimensionality. Another useful measure of the density is the Wigner-Seitz radius

$$r_s = \left(\frac{3}{4\pi n} \right)^{1/3} = 1.919/k_F \quad (5.6)$$

Regions of high density, such as core electrons, have average $r_s < 1$, valence electrons have average r_s between about 1 and 6. We find

$$T_s^{\text{loc}}[n] = \frac{3}{10} \int d^3r k_F^2(\mathbf{r}) n(\mathbf{r}) = A_s \int d^3r n^{5/3}(\mathbf{r}) \quad (5.7)$$

where $A_s = (3/10)(3\pi^2)^{2/3} = 2.871$. Evaluation of the Fock integral Eq. (3.40) for a Slater determinant of orbitals yields the exchange energy per electron of a uniform gas as

$$\epsilon_x^{\text{unif}}(n) = 3k_F/4\pi, \quad (5.8)$$

leading to

$$E_x^{\text{LDA}}[n] = A_x \int d^3r n^{4/3}(\mathbf{r}) \quad (5.9)$$

where $A_x = -(3/4)(3/\pi)^{1/3} = -0.738$.

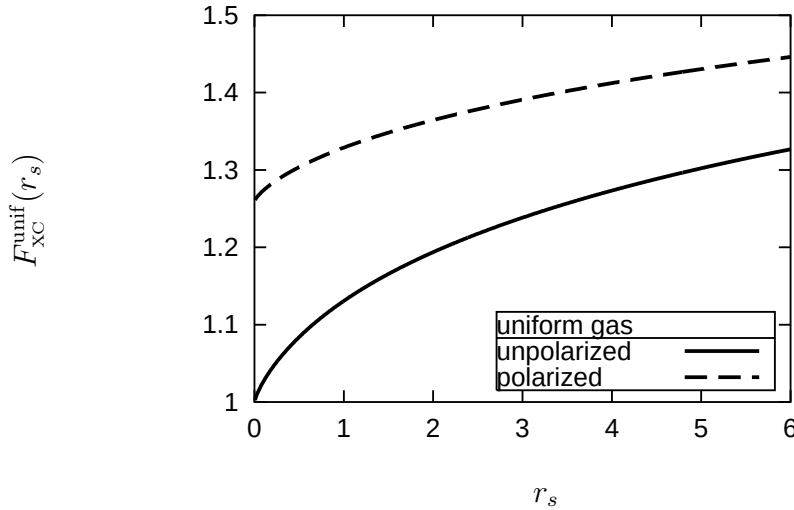


Figure 5.2: Enhancement factor for correlation in a uniform electron gas as a function of Wigner-Seitz radius for unpolarized (solid line) and fully polarized (dashed line) cases.

Correlation is far more sophisticated, as it depends explicitly on the physical ground-state wavefunction of the uniform gas. A simple way to represent it is simply an enhancement factor over exchange:

$$\epsilon_{\text{xc}}^{\text{unif}}(r_s) = F_{\text{xc}}(r_s)\epsilon_{\text{x}}^{\text{unif}}(r_s) \quad (5.10)$$

and this enhancement factor is plotted in Fig. 5.2. There are several important features to the curve:

- At $r_s = 0$, exchange dominates over correlation, and $F_{\text{x}} = 1$.
- As $r_s \rightarrow 0$, there is a sharp dive toward 1. This is due to the long-ranged nature of the Coulomb repulsion in an infinite system, leading to

$$\epsilon_{\text{c}}^{\text{unif}}(r_s) \rightarrow 0.0311 \ln r_s - 0.047 + 0.009r_s \ln r_s - 0.017r_s \quad (r_s \rightarrow 0) \quad (5.11)$$

- In the large r_s limit (low-density)

$$\epsilon_{\text{c}}^{\text{unif}}(r_s) \rightarrow -d_0/r_s - d_1/r_s^{3/2} - \dots \quad (r_s \rightarrow \infty) \quad (5.12)$$

The constant $d_0 = \dots$ was first deduced by Wigner from the Wigner crystal for this system. Note that this means correlation behaves the same way as exchange here, and so $F_{\text{xc}}^{\text{unif}}(r_s \rightarrow \infty) = X$.

- The approach to the low-density limit is extremely slow.

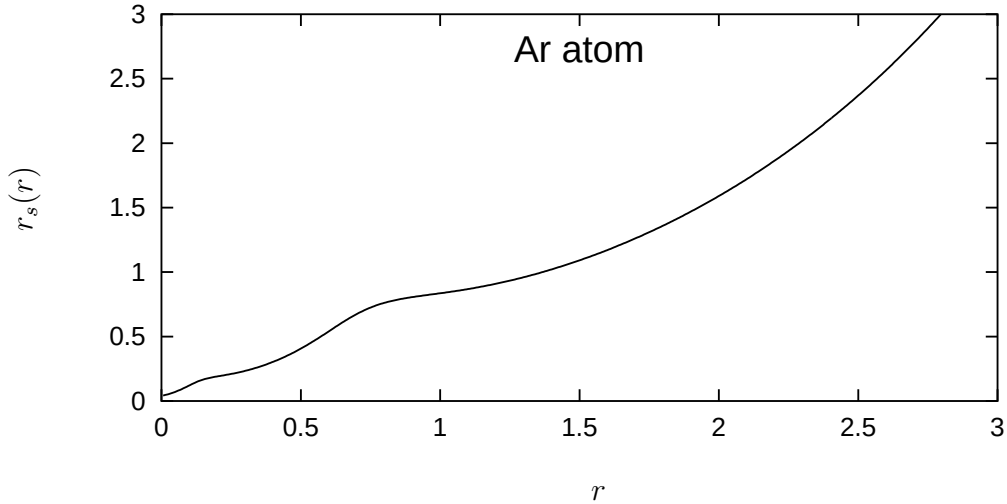


Figure 5.3: $r_s(r)$ in Ar atom.

Over the years, this function has become very well-known, by combining limiting information like that above, with accurate quantum Monte Carlo data for the uniform gas. An early popular formula in solid-state physics is PZ81, while the parametrization of Vosko-Wilkes-Nusair (VWN) has been implemented in quantum chemical codes. Note that in the Gaussian codes, VWN refers to an older formula from the VWN paper, while

VWN-V is the actual parametrization recommended by VWN. More recently, Perdew and Wang reparametrized the data. These accurate parametrizations differ only very slightly among themselves.

5.3 Density analysis for real atoms, molecules, and solids

Recall the radial density plot of the Ar atom, Fig. 3.2. Next, we plot the local Wigner-Seitz radius, $r_s(r)$, in Fig. 5.3, and find that the shells are less obvious. The core electrons have $r_s \leq 1$, while the valence electrons have $r_s \geq 1$, with a tail stretching toward $r_s \rightarrow \infty$. To see the distribution of densities better, we define the *density of r_s 's*:

$$g_1(r_s) = \int d^3r \, n(\mathbf{r}) \, \delta(r_s - r_s(\mathbf{r})). \quad (5.13)$$

This has the simple interpretation: $g(r_s)dr_s$ is the number of electrons in the system with Seitz radius between r_s and $r_s + dr_s$, and so satisfies:

$$\int_0^\infty dr_s \, g(r_s) = N. \quad (5.14)$$

This is plotted in Fig. 5.4. The different peaks represent the s electrons in each shell.

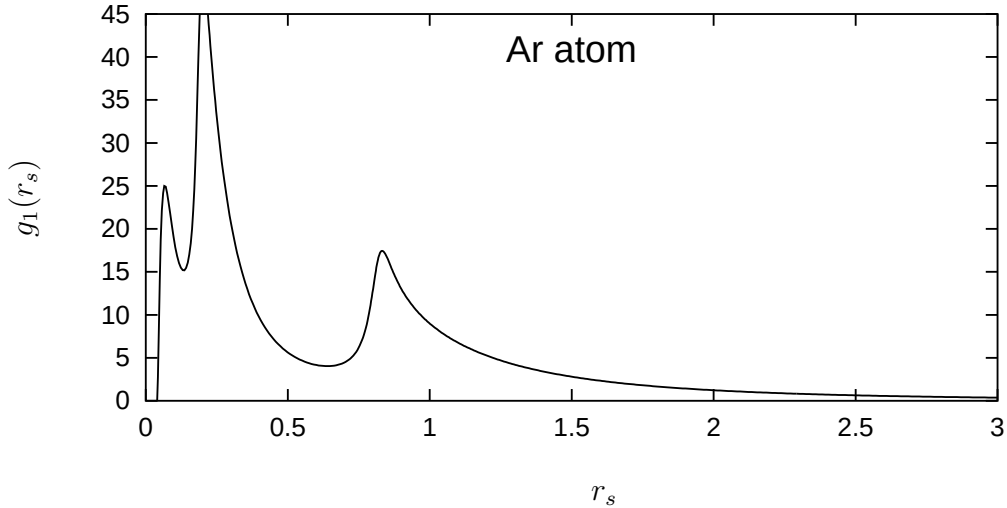


Figure 5.4: $g_1(r_s)$ in Ar atom.

If we integrate this function forward from $r_s = 0$, we find that it reaches 2 at $r_s = 0.15$, 4 at 0.41, 10 at 0.7, and 12 at 0.88; these numbers represent (roughly) the maximum r_s in a given shell. The 1s core electrons live with $r_s \leq 1.5$, and produce the first peak in g_1 ; the 2s produce the peak at $r_s = 0.2$, and the 2p produce no peak, but stretch the 2s peak upto 0.7. The peak at about 0.82 is the 3s electrons, and the long tail includes the 3p electrons.

Why is this analysis important? We usually write

$$E_{\text{xc}}^{\text{LDA}} = \int d^3r \, n(\mathbf{r}) \, \epsilon_{\text{xc}}^{\text{unif}}(r_s(\mathbf{r})), \quad (5.15)$$

where $\epsilon_{\text{xc}}^{\text{unif}}$ is the exchange-correlation energy per particle in the uniform gas. But armed with our analysis, we may rewrite this as

$$E_{\text{xc}}^{\text{LDA}} = \int_0^\infty dr_s g(r_s) \epsilon_{\text{xc}}^{\text{unif}}(r_s). \quad (5.16)$$

Thus the contribution to $E_{\text{xc}}^{\text{LDA}}$ for a given r_s value is given by $g_1(r_s)$ times the weighting factor $\epsilon_{\text{xc}}^{\text{unif}}(r_s)$. Clearly, from Fig. 5.4, we see that, to get a good value for the exchange-correlation energy of the Ar atom, LDA must do well for $r_s \leq 2$, but its performance for larger r_s values is irrelevant.

Typical r_s values are small for core electrons (at the origin, a hydrogenic atom has $r_s = 0.72/Z$), but valence electrons have r_s between about 1 and 6. These produce the dominant contribution to chemical processes, such as atomization of molecules, but core relaxations with $r_s \ll 1$ can also contribute. The valence electrons in simple metal solids have r_s between 2 and 6.

5.4 Performance of LDA

The local density approximation to exchange-correlation was introduced by Kohn and Sham in 1965, and has been one of the most successful approximations ever. Until the early 90's, it was the standard approach for all density functional calculations, which were denoted *ab initio* in solid state physics. It remains perhaps the most reliable approximation we have.

For atoms and molecules, the total exchange energy is typically underestimated by about 10%. On the other hand, the correlation energy is overestimated by about a factor of 2 or 3. Since for many systems of physical and chemical interest, exchange is about 10 times bigger than correlation, the overestimate of correlation complements the underestimate of exchange, and the net exchange-correlation energy is typically underestimated by about 7%.

The self-consistent density in such calculations is always close to the exact density, being hard to distinguish by eye. The exchange-correlation potentials, however, look very different from the exact quantities for finite systems, as shown in Fig. 6.2). This in turn means that the orbital eigenvalues can be very different from exact Kohn-Sham eigenvalues. On the other hand, for solids, these eigenvalues are often plotted as the band structure in solid-state texts. In these cases, the overall shape and position is good, but the band gap, between HOMO and LUMO, is consistently underestimated by at least a factor of 2. In some cases, some semiconductors have no gap in LDA, so it makes the incorrect prediction that they are metals.

For atomization energies of molecules or cohesive energies of solids, LDA tends to overbind by about 30 kcal/mol, or 1.3 eV, or about 50 millihartrees. This meant it was not adopted as a general tool in quantum chemistry at the time. For similar reasons, this also leads to transition state barriers that are too low, often non-existent. In solid state

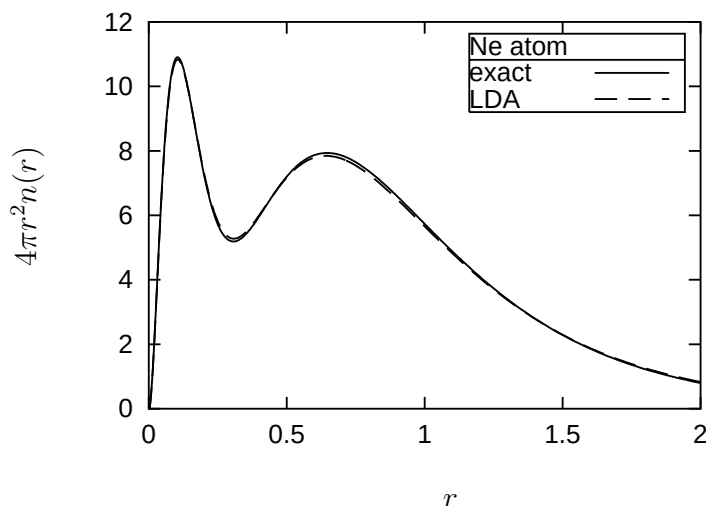


Figure 5.5: Radial density of the Ne atom, both exactly and from an LDA calculation

physics, an infamous failure is the prediction that the non-magnetic structure of iron is of slightly lower energy than the magnetic one. Similarly, ionization potentials, especially those involving a change in angular momentum of the system, are often not well-described by LDA. However, bond lengths are extremely good in LDA, usually (but not always) being underestimated by about 1-2

Finally, qualitative errors occur for highly correlated systems, such as the solid NiO or the molecules Cr_2 , or H_2 stretched to large distances. These systems are extremely difficult to study with density functional approximations, as will be discussed below.

Must add much more discussion here, especially for magnetic materials...

5.5 Questions about the local density approximation

1. Following the previous question, can you deduce the asymptotic form of the exchange-correlation potential, i.e., $v_{\text{xc}}(\mathbf{r})$ as $r \rightarrow \infty$? Would a local approximation capture this behavior? (See section 8.5).
2. Deduce the formula of $T_{\text{s}}^{\text{loc}}$ for unpolarized electrons in a one-dimensional box.

Discussion

1. For spin-unpolarized electrons in the box, there will be twice as many electrons for a given density, as each orbital will be doubly occupied. Thus $k_F = \pi n/2$, and $T_{\text{s}}^{\text{loc}}[n] = (\pi^2/24) \int dx n^3(x)$. We will see in chapter ?? how to find the exact spin scaling of any orbital functional.

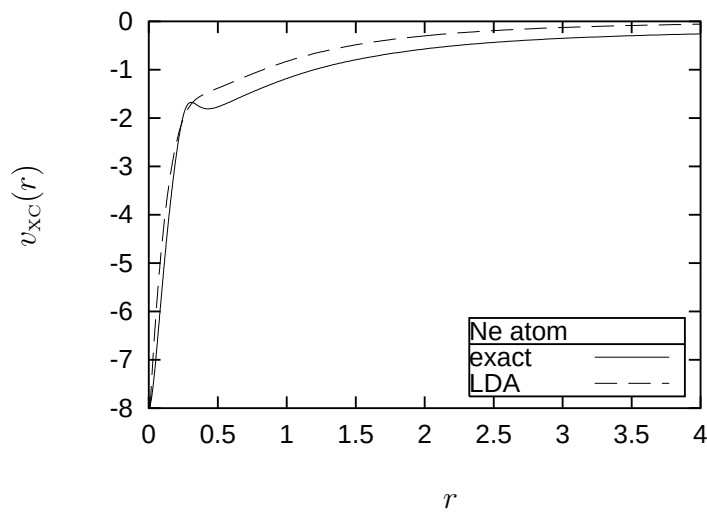


Figure 5.6: Exchange-correlation potential of Ne atom, both exactly and in LDA.

Chapter 6

Spin density functional theory

6.1 Kohn-Sham equations in SDFT

We next introduce spin density functional theory, a simple generalization of density functional theory. We consider the up and down densities as separate variables, defined as

$$n_{\sigma}(\mathbf{r}) = N \int dx_2 \dots \int dx_N |\Psi(\mathbf{r}, \sigma, x_2, \dots, x_N)|^2, \quad (6.1)$$

with the interpretation that $n_{\sigma}(\mathbf{r})d^3r$ is the probability for finding an electron of spin σ in d^3r around $\mathbf{r}$. Then the Hohenberg-Kohn theorems can be proved, showing a one-to-one correspondence between spin densities and spin-dependent external potentials, $v_{\text{ext},\sigma}(\mathbf{r})$. Similarly, the Kohn-Sham equations can be developed with spin-dependent Kohn-Sham potentials. All modern density functional calculations are in fact spin-density functional calculations. This has several advantages:

1. Systems in collinear magnetic fields are included.
2. Even when the external potential is not spin-dependent, it allows access to magnetic response properties of a system.
3. Even if not interested in magnetism, we will see that the increased freedom in spin DFT leads to more accurate functional approximations for systems that are spin-polarized, e.g., the Li atom.

We will see in the next chapter that it is straightforward to turn some density functionals into spin-density functionals, while others are more complicated.

6.2 Spin scaling

We can easily deduce the spin scaling of orbital functionals, while little is known of the exact spin-scaling of correlation in general. We do spin-scaling of the kinetic energy functional as an example. Suppose we know $T_s[n]$ as a density functional for spin-unpolarized

systems. Then, for an orbital-based functional, we know

$$T_s[n_\uparrow, n_\downarrow] = T_s[n_\uparrow, 0] + T_s[0, n_\downarrow] \quad (6.2)$$

i.e., the contributions come from each spin separately. Applying this to the spin-unpolarized case, we find

$$T_s[n] = T_s[n/2, n/2] = 2T_s[n/2, 0] \quad (6.3)$$

or $T_s[n, 0] = T_s[2n]/2$. Inserting this result back into Eq. (6.2), we find

$$T_s[n_\uparrow, n_\downarrow] = \frac{1}{2} (T_s[2n_\uparrow] + T_s[2n_\downarrow]) \quad (6.4)$$

An analogous formula is true for the spin-scaling of exchange.

The local spin density (LSD) approximation is the spin-scaled generalization of LDA. The formulas for the kinetic and exchange energies are straightforward (see exercise below), but the correlation energy, as a function of spin-polarization, for the uniform gas, must be extracted from QMC and known limits. We denote the relative spin polarization at any point in the system by

$$\zeta(\mathbf{r}) = (n_\uparrow(\mathbf{r}) - n_\downarrow(\mathbf{r}))/n(\mathbf{r}) \quad (6.5)$$

Typically, when a system is polarized, exchange keeps the electrons further apart, reducing the correlation energy, but this has not been proven generally.

Exercise 28 LSD

Find the spin-scaling formulas for T_s and E_x within the local approximation, and test them on both the hydrogen atom and the three-dimensional harmonic oscillator. Comment on your results relative to LDA.

6.3 Polarizing the uniform electron gas

6.4 Performance of LSD

The local density approximation to exchange-correlation was introduced by Kohn and Sham in 1965, and has been one of the most successful approximations ever. Until the early 90's, it was the standard approach for all density functional calculations, which were denoted *ab initio* in solid state physics. It remains perhaps the most reliable approximation we have.

For atoms and molecules, the total exchange energy is typically underestimated by about 10%. On the other hand, the correlation energy is overestimated by about a factor of 2 or 3. Since for many systems of physical and chemical interest, exchange is about 10 times bigger than correlation, the overestimate of correlation compliments the underestimate of exchange, and the net exchange-correlation energy is typically underestimated by about 7%.

The self-consistent density in such calculations is always close to the exact density, being hard to distinguish by eye. The exchange-correlation potentials, however, look

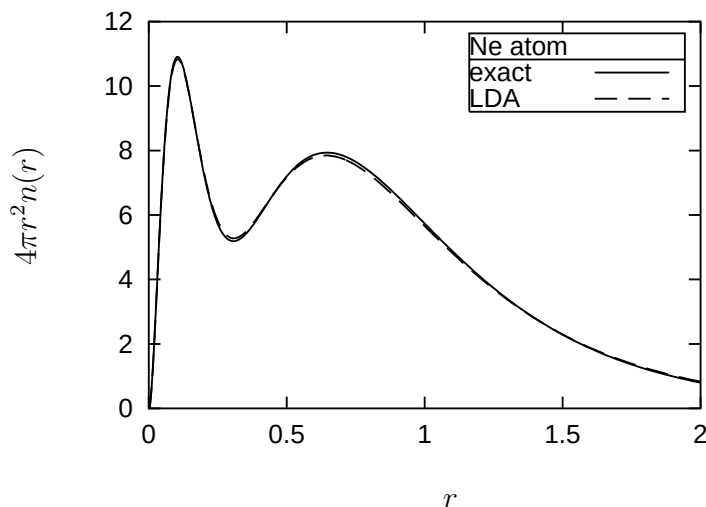


Figure 6.1: Radial density of the Ne atom, both exactly and from an LDA calculation

very different from the exact quantities for finite systems, as shown in Fig. 6.2). This

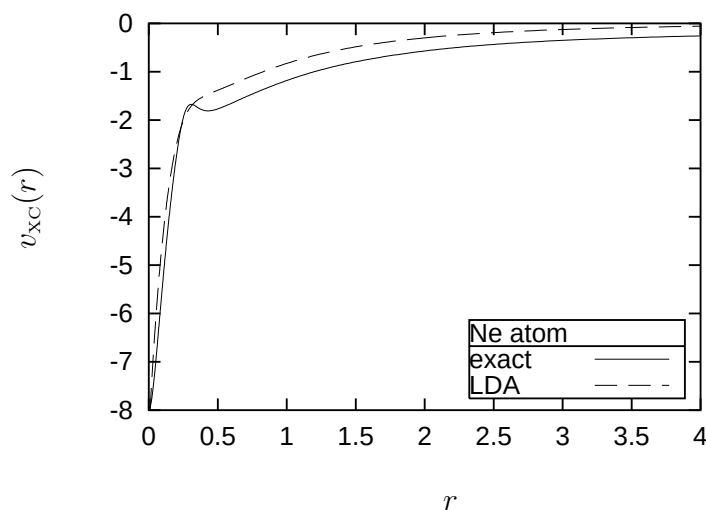


Figure 6.2: Exchange-correlation potential of Ne atom, both exactly and in LDA.

in turn means that the orbital eigenvalues can be very different from exact Kohn-Sham eigenvalues. Thus ionization potentials from orbital energy differences are very poor. This will be discussed in great detail below. On the other hand, for solids, these eigenvalues are often plotted as the band structure in solid-state texts. In these cases, the overall shape and position is good, but the band gap, between HOMO and LUMO, is consistently underestimated by at least a factor of 2. In some cases, some semiconductors have no gap in LDA, so it makes the incorrect prediction that they are metals.

For atomization energies of molecules or cohesive energies of solids, LDA tends to overbind by about 30 kcal/mol, or 1.3 eV, or about 50 millihartrees. This meant it was not adopted as a general tool in quantum chemistry at the time. For similar reasons, this also leads to transition state barriers that are too low, often non-existent. In solid state physics, an infamous failure is the prediction that the non-magnetic structure of iron is of slightly lower energy than the magnetic one. Similarly, ionization potentials, especially those involving a change in angular momentum of the system, are often not well-described by LDA. However, bond lengths are extremely good in LDA, usually (but not always) being underestimated by about 1-2

Finally, qualitative errors occur for highly correlated systems, such as the solid NiO or the molecules Cr_2 , or H_2 stretched to large distances. These systems are extremely difficult to study with density functional approximations, as will be discussed below.

6.5 Questions about spin density functional theory

1. Why does LSD yield a more accurate energy for the Hydrogen atom than LDA?
2. State in words the relation between $v_s[n](\mathbf{r})$ and $v_{s\sigma}[n_\uparrow, n_\downarrow](\mathbf{r})$. When do they coincide?
3. Does the reliability of LSD show that most systems are close to uniform?

Chapter 7

Some exact conditions satisfied by LDA

¹ In this chapter, we review several known exact conditions, not based on coordinate scaling, and see how well LDA meets these conditions.

7.1 Size consistency

An important exact property of any electronic structure method is size consistency. Imagine you have a system which consists of two extremely separated pieces of matter, called A and B. Then a size-consistent treatment should yield the same total energy, whether the two pieces are treated separately or as a whole, i.e., $E_{A+B} = E_A + E_B$. Configuration interaction calculations with a finite order of excitations are *not* size-consistent, but coupled-cluster calculations are. Most density functionals are size-consistent, but some with explicit dependence on N are not.

7.2 Lieb-Oxford bound

Another exact inequality for the potential energy contribution to the exchange-correlation functional is the Lieb-Oxford bound:

$$U_{xc}[n] \geq C_{LO} E_x^{LDA}[n] \quad (7.1)$$

where $C_{LO} \leq 2.273$.

Exercise 29 Lieb-Oxford bound

What does the Lieb-Oxford bound tell you about $\epsilon_c^{\text{unif}}(r_s)$? Does LDA respect the Lieb-Oxford bound?

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7.3 Uniform coordinate scaling for one electron

It will prove very useful to figure out what happens to various quantities when the coordinates are scaled, i.e., when x is replaced by γx everywhere in a problem, with γ a positive number. For one electron in one dimension, we define the scaled wavefunction as

$$\phi_\gamma(x) = \gamma^{\frac{1}{2}} \phi(\gamma x), \quad 0 < \gamma < \infty, \quad (7.2)$$

where the scaling factor out front has been chosen to preserve normalization:

$$1 = \int_{-\infty}^{\infty} dx |\phi(x)|^2 = \int_{-\infty}^{\infty} dx \gamma |\phi(\gamma x)|^2 = \int_{-\infty}^{\infty} dx' |\phi(x')|^2. \quad (7.3)$$

A scale factor of $\gamma > 1$ will squeeze the wavefunction, and of $\gamma < 1$ will stretch it out. For example, consider $\phi(x) = \exp(-|x|)$. Then $\phi_\gamma(x) = \sqrt{\gamma} \exp(-\gamma|x|)$ is a different wavefunction for every γ . For example, $\phi_2(x) = \sqrt{2} \exp(-2|x|)$. In Fig. 7.1, we sketch a

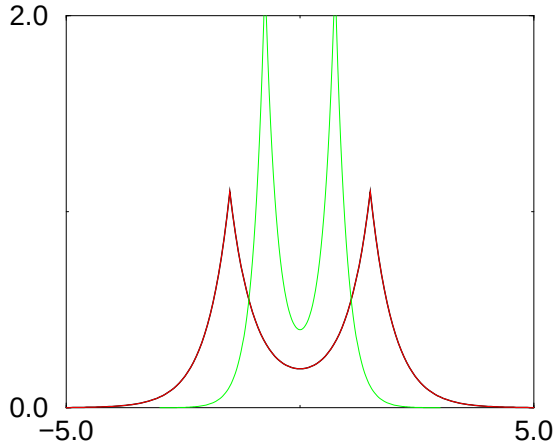


Figure 7.1: Cartoon of the one-dimensional H_2 molecule density, and scaled by a factor of 2.

density for the one-dimensional H_2 molecule of a previous exercise, and the same density scaled by $\gamma = 2$,

$$n_\gamma(x) = \gamma n(\gamma x). \quad (7.4)$$

Note how $\gamma > 1$ squeezes the density toward the origin, keeping the number of electrons fixed. We always use subscripts to denote a function which has been scaled.

What is the kinetic energy of such a scaled wave-function?

$$T[\phi_\gamma] = \frac{1}{2} \int_{-\infty}^{\infty} dx |\phi'_\gamma(x)|^2 = \frac{\gamma}{2} \int_{-\infty}^{\infty} dx |\phi'(\gamma x)|^2 = \frac{\gamma^2}{2} \int_{-\infty}^{\infty} dx' |\phi'(x')|^2 = \gamma^2 T[\phi], \quad (7.5)$$

i.e., the kinetic energy grows quadratically with γ . The potential energy is not so straightforward in general, because it is not a universal functional:

$$V[\phi_\gamma] = \int_{-\infty}^{\infty} dx |\phi_\gamma(x)|^2 V(x) = \int_{-\infty}^{\infty} dx' |\phi(x')|^2 V\left(\frac{x}{\gamma}\right) = \langle V(x/\gamma) \rangle \quad (7.6)$$

However, if the potential energy is homogeneous of degree p , i.e.,

$$V(\gamma x) = \gamma^p V(x), \quad (7.7)$$

then

$$V[\phi_\gamma] = \gamma^{-p} V[\phi]. \quad (7.8)$$

Consider any set of trial wavefunctions. If scaling any member of the set leads to another member of the set, then we say that the set *admits* scaling.

Exercise 30 Scaling of trial wavefunctions

Do the sets of trial wavefunctions in Ex. 11 admit scaling?

The only important change when going to three dimensions for our purposes in the preceding discussion is that the scaling normalization factors change:

$$\phi_\gamma(\mathbf{r}) = \gamma^{\frac{3}{2}} \phi(\gamma \mathbf{r}) \quad n_\gamma(r) = \gamma^3 n(\gamma r) \quad (7.9)$$

7.4 Coordinate scaling of density functionals

Now we turn our attention to density functionals. Functionals defined in terms of the Kohn-Sham wavefunction are far simpler than those including correlation effects. In particular, there is both the non-interacting kinetic energy and the exchange energy. We shall see that both their uniform scaling and their spin-scaling are straightforward.

Consider uniform scaling of an N -electron wavefunction,

$$\Psi_\gamma(\mathbf{r}_1, \dots, \mathbf{r}_N) = \gamma^{3N/2} \Psi(\gamma \mathbf{r}_1, \dots, \gamma \mathbf{r}_N). \quad (7.10)$$

The scaled wavefunction has density $n_\gamma(\mathbf{r})$. A key question is: Does $\Psi[n_\gamma] = \Psi_\gamma[n]$? We show below that this is *not* true for the physical wavefunction, but *is* true for the Kohn-Sham wavefunction. Consider the latter case first. We already know that $T_s[\Phi_\gamma] = \gamma^2 T_s[\Phi]$. Thus if Φ minimizes T_s and yields density n , then Φ_γ also minimizes T_s , but yields density n_γ . Therefore, Φ_γ is the Kohn-Sham wavefunction for n_γ , or

$$\Phi_\gamma[n] = \Phi[n_\gamma]. \quad (7.11)$$

This result is central to understanding the behaviour of the non-interacting kinetic and exchange energies. We can immediately use it to see how they scale, since we can turn density functionals into orbital functionals, and vice versa:

$$T_s[n_\gamma] = T_s[\Phi[n_\gamma]] = T_s[\Phi_\gamma[n]] = \gamma^2 T_s[\Phi[n]] = \gamma^2 T_s[n], \quad (7.12)$$

and

$$E_x[n_\gamma] = E_x[\Phi[n_\gamma]] = E_x[\Phi_\gamma[n]] = \gamma E_x[\Phi[n]] = \gamma E_x[n]. \quad (7.13)$$

These exact conditions are utterly elementary, saying only that if the length scale of a system changes, these functionals should change in a trivial way. Any approximation to

these functionals must therefore satisfy these relations. However, they are also extremely powerful in limiting the possible forms functional approximations can have.

The next exercise shows us that scaling relations determine the functional forms of the local approximation to these simple functionals, and the uniform electron gas is referred to only for the values of the coefficients.

Exercise 31 Local density approximations for T_s and E_x :

Show that, in making a local approximation for three-dimensional systems, the power of the density in both the non-interacting kinetic and exchange energy approximations are determined by scaling considerations.

This reasoning breaks down when correlation is included, because this involves energies evaluated on the physical wavefunction. As mentioned above, a key realization there is that the scaled ground-state wavefunction is not the ground-state wavefunction of the scaled density, because the physical wavefunction minimizes both T and V_{ee} simultaneously. However, we can still use the variational principle to deduce an inequality. We write

$$F[n_\gamma] = \langle \Psi[n_\gamma] | (\hat{T} + \hat{V}_{ee}) | \Psi[n_\gamma] \rangle \leq \langle \Phi_\gamma[n] | (\hat{T} + \hat{V}_{ee}) | \Phi_\gamma[n] \rangle \quad (7.14)$$

or

$$F[n_\gamma] \leq \gamma^2 T[n] + \gamma V_{ee}[n] \quad (7.15)$$

This is the fundamental inequality of uniform scaling, as it tells us inequalities about how correlation contributions scale.

To see an example, apply Eq. (7.15) to $n' = n_\gamma$ and write $\gamma' = 1/\gamma$, to yield

$$F[n'] \leq T[n'_\gamma]/\gamma'^2 + V_{ee}[n'_\gamma]/\gamma'. \quad (7.16)$$

But we can just drop the primes in this equation, and multiply through by γ , and add $(\gamma^2 - \gamma)T[n]$ to both sides:

$$\gamma^2 T[n] + \gamma V_{ee}[n] \leq T[n_\gamma]/\gamma + V_{ee}[n_\gamma] + (\gamma^2 - \gamma)T[n]. \quad (7.17)$$

Now the left-hand-side equals the right-hand-side of Eq. (7.15), so we can combine the two equations, to find

$$(\gamma - 1) T[n_\gamma] \leq \gamma^2 (\gamma - 1) T[n]. \quad (7.18)$$

Note that for $\gamma > 1$, we can cancel $\gamma - 1$ from both sides, to find $T[n_\gamma] < \gamma^2 T[n]$. As we scale the system to high density, the physical kinetic energy grows less rapidly than the non-interacting kinetic energy. For $\gamma < 1$, the reverse is true, i.e.,

$$T[n_\gamma] \leq \gamma^2 T[n] \quad \gamma > 1, \quad T[n_\gamma] \geq \gamma^2 T[n] \quad \gamma < 1. \quad (7.19)$$

Exercise 32 Scaling V_{ee}

Show

$$V_{ee}[n_\gamma] \geq \gamma V_{ee}[n] \quad \gamma > 1, \quad V_{ee}[n_\gamma] \leq \gamma V_{ee}[n] \quad \gamma < 1. \quad (7.20)$$

These inequalities actually provide very tight bounds on these large numbers. But of greater interest are the much smaller differences with Kohn-Sham values, i.e., the correlation contributions. So

Exercise 33 Scaling E_C

Show

$$E_C[n_\gamma] \geq \gamma E_C[n], \quad \gamma > 1, \quad E_C[n_\gamma] \leq \gamma E_C[n], \quad \gamma < 1, \quad (7.21)$$

and

$$T_C[n_\gamma] \leq \gamma^2 T_C[n], \quad \gamma > 1, \quad T_C[n_\gamma] \geq \gamma^2 T_C[n], \quad \gamma < 1. \quad (7.22)$$

Exercise 34 Scaling inequalities for LDA

Give a one-line argument for why LDA must satisfy the scaling inequalities for correlation energies.

In fact, for most systems we study, both E_C and T_C are relatively insensitive to scaling the density toward the high-density limit, so these inequalities are less useful.

The correlation energy is believed to have the following expansion under scaling to the low-density limit:

$$E_C[n_\gamma] = \gamma B[n] + \gamma^{3/2} C[n] + \dots, \quad \gamma \rightarrow 0 \quad (7.23)$$

This is satisfied within LDA, as seen from Eqs. (??). But most systems of chemical interest are closer to the high-density limit (see section ??), where LDA fails.

Exercise 35 Extracting exchange

If someone gives you an exchange-correlation functional $E_{xc}[n]$, define a procedure for extracting the exchange contribution.

7.5 Virial theorem

Any eigenstate wavefunction extremizes the expectation value of the Hamiltonian. Thus any small variations in such a wavefunction lead only to second order changes, i.e.,

$$E[\phi_{sol} + \delta\phi] = E[\phi_{sol}] + O(\delta\phi^2). \quad (7.24)$$

Assume ϕ is the ground-state wavefunction of $\hat{H}$. Then ϕ_γ is not, except at $\gamma = 1$. But small variations in γ near 1 lead only to second order changes in $\langle \hat{H} \rangle$, so

$$\left. \frac{d}{d\gamma} \right|_{\gamma=1} \langle \phi_\gamma | \hat{H} | \phi_\gamma \rangle = 0. \quad (7.25)$$

But, from Eq. (7.5), $dT[\phi_\gamma]/d\gamma = 2\gamma T[\phi]$, and from Eq. (7.6), $dV[\phi_\gamma]/d\gamma = -\gamma^{-2} \langle x \frac{dV}{dx} \rangle$ at $\gamma = 1$, yielding

$$2T = \langle x \frac{dV}{dx} \rangle. \quad (7.26)$$

The right-hand side is called the virial of the potential. So this must be satisfied by any solution to the Schrödinger equation, and can be used to test how accurately an approximate solution satisfies it.

Note that this is true for *any* eigenstate and even for any approximate solution, once that solution is a variational extremum over a class of wave-functions which admits scaling, i.e., a class in which coordinate scaling of any member of the class yields another member of that class. Linear combinations of functions do not generally form a class which admits scaling.

Exercise 36 Using the virial theorem

Of the exercises we have done so far, which approximate solutions satisfy the virial theorem Eq. (7.26) exactly, and which do not? What can you deduce in the two different cases?

We now derive equivalent formulae for the density functional case. We will first generalize Eq. (7.24), and then Eq. (7.26). As always, instead of considering the ground-state energy itself, we consider just the construction of the universal functional $F[n]$. Write $\hat{F} = \hat{T} + \hat{V}_{\text{ee}}$. Then

$$F[n] = \langle \Psi[n] | \hat{F} | \Psi[n] \rangle, \quad (7.27)$$

and, if we insert any other wavefunction yielding the density $n(\mathbf{r})$, we must get a higher number. Consider especially the wavefunctions $\Psi_\gamma[n_{1/\gamma}]$. These yield the same density, but are not the minimizing wavefunctions. Then

$$\frac{d}{d\gamma} \Big|_{\gamma=1} \langle \Psi_\gamma[n_{1/\gamma}] | \hat{F} | \Psi_\gamma[n_{1/\gamma}] \rangle = 0. \quad (7.28)$$

But expectation values of operators scale very simply when the wavefunction is scaled, so that

$$\frac{d}{d\gamma} \Big|_{\gamma=1} \left(\gamma^2 T[n_{1/\gamma}] + \gamma V_{\text{ee}}[n_{1/\gamma}] \right) = 0, \quad (7.29)$$

or, swapping γ to $1/\gamma$ in the derivative,

$$2T[n] + V_{\text{ee}}[n] = \frac{d}{d\gamma} \Big|_{\gamma=1} (T[n_\gamma] + V_{\text{ee}}[n_\gamma]). \quad (7.30)$$

This then is the generalization of Eq. (7.24) for density functional theory: Because $\Psi[n]$ minimizes $\hat{F}$, variations induced by scaling (but keeping the density fixed) have zero derivative around the solution, leading to Eq. (7.30).

As always, we reduce this to a statement about exchange-correlation by applying it to both the interacting and Kohn-Sham systems:

$$E_{\text{xc}}[n] + T_{\text{c}}[n] = dE_{\text{xc}}[n_\gamma]/d\gamma \Big|_{\gamma=1} \quad (7.31)$$

Exercise 37 Virial expressed as scaling derivative

Prove Eq. (7.31).

After our earlier warm-up exercises, it is trivial to derive the virial theorem for the exchange-correlation potential. For an arbitrary system, the virial theorem for the ground-state yields:

$$2T = \sum_{i=1}^N \langle \Psi | \mathbf{r}_i \cdot \nabla_i \hat{V} | \Psi \rangle, \quad (7.32)$$

no matter what the external potential. For our problems, the electron-electron repulsion is homogeneous of order -1, and so

$$2T + V_{\text{ee}} = \int d^3r \, n(\mathbf{r}) \mathbf{r} \cdot \nabla v_{\text{ext}}(\mathbf{r}). \quad (7.33)$$

This theorem applies equally to the non-interacting and interacting systems, and by subtracting the difference, we find

$$E_{\text{xc}}[n] + T_{\text{c}}[n] = - \int d^3r \, n(\mathbf{r}) \mathbf{r} \cdot \nabla v_{\text{xc}}(\mathbf{r}). \quad (7.34)$$

Since we can either turn off the coupling constant or scale the density toward the high-density limit, this applies separately to the exchange contributions to both sides, and the remaining correlation contributions.

For almost any approximate functional, once a Kohn-Sham calculation has been cycled to self-consistency, Eq. (7.34) will be satisfied. It is thus a good test of the convergence of such calculations, but is rarely performed in practice.

Exercise 38 Virial for LDA:

Show that the virial theorem is satisfied in an LDA calculation.

7.6 Questions about some exact conditions satisfied by LDA.

1. What is the effect of having nuclear charge $Z \neq 1$ for the 1-d H-atom?
2. Is the virial theorem satisfied for the ground-state of the problem $V(x) = -\exp(-|x|)$?
3. Why does LDA satisfy the Lieb-Oxford bound?
4. For a homogeneous potential of degree p , e.g., $p=-1$ for the delta function well, we know $E = -T$. Can we find the ground-state by simply maximizing T ?
5. What is the exact kinetic energy *density* functional for one electron in one-dimension? How does it scale?
6. Does $T_{\text{s}}^{\text{loc}}[n]$ from chapter ?? satisfy the correct scaling relation? (Recall question 1 from chapter ??).
7. If Ψ is the ground-state for an interacting electronic system of potential $v_{\text{ext}}(\mathbf{r})$, what is Ψ_{γ} a ground-state of?

Chapter 8

Some exact conditions not satisfied by LDA

8.1 High-density limit of correlation

Levy has shown that for finite systems, $E_C[n_\gamma]$ tends to a negative constant as $\gamma \rightarrow \infty$. From Fig. 8.1, we see that for the He atom E_C varies little with scaling.

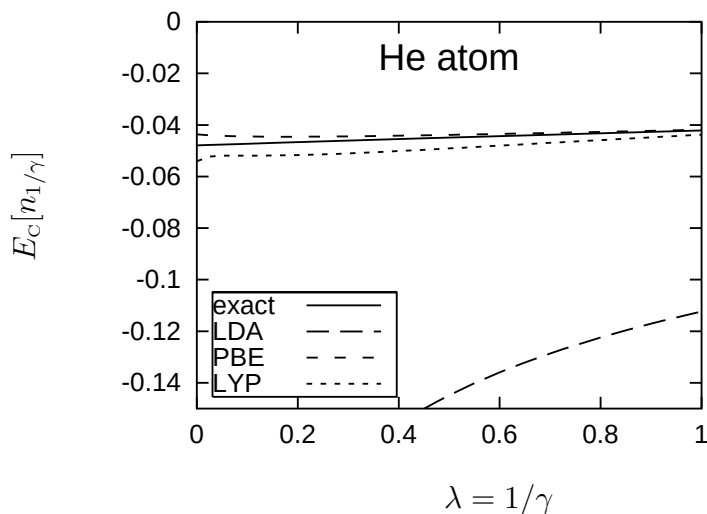


Figure 8.1: Correlation energy of the He atom, both exactly and within several functional approximations, as the density is squeezed.

We may write power series for $E_C[n_\gamma]$ around the high-density limit:

$$E_C[n_\gamma] = E_C^{(2)}[n] + E_C^{(3)}[n]/\gamma + \dots, \quad \gamma \rightarrow \infty \quad (8.1)$$

From the figure, we see that for the He atom, as is the case with most systems of chemical interest, $E_C[n_\gamma]$ is almost constant, and very close to linear in $1/\gamma$, showing that the system is close to the high-density limit. The high-density property is *violated* by LDA (see the

figure), because of the logarithmic divergence introduced by the Coulomb repulsion in an extended system, as we saw in Chapter 5. Thus the LDA curve in the figure diverges at $\gamma \rightarrow 0$, another way to understand the LDA overestimate of correlation for finite systems.

8.2 Self-interaction error and H_2^+

For any one electron system, $V_{ee} = 0$, so that $E_x = -U$, and $E_c = 0$. This is one of the most difficult properties for density functionals to get right. This error is called the self-interaction error, as it can be thought of as arising from the interaction of the charge density with itself in U , not being correctly cancelled by E_x and E_c . Similarly, as we have already seen, $E_x = -U/2$ for two spin-unpolarized electrons.

Exercise 39 Fermi-Amaldi correction

An approximation for the exchange energy is $E_x[n] = -U[n]/N$. This is exact for one or two (spin-unpolarized) electrons. Show that it is not size-consistent.

This problem becomes acute when there is more than one center in the external potential. Consider, e.g. H_2^+ . As the nuclear separation grows from zero, the charge density spreads out, so that a local approximation produces a smaller and smaller fraction of the correct result.

Exercise 40 Stretched H_2^+

Calculate the LSD error in the exchange energy of H_2^+ in the limit of infinite separation.

8.3 Symmetry dilemma and stretched H_2

Another infamous difficulty of DFT goes all the way back to the first attempts to understand H_2 using quantum mechanics. In the absence of a magnetic field, the ground state of two electrons is always a singlet. At the chemical bond length, a Hartree-Fock single Slater determinant is a reasonable approximation to the true wavefunction, and yields roughly accurate numbers:

$$\Phi^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2) = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2) \approx \Psi(\mathbf{r}_1, \mathbf{r}_2) \quad (8.2)$$

However, when the bond is stretched to large distances, the correct wavefunction becomes a linear combination of two Slater determinants (the Heitler-London wavefunction), one for each electron on each H-atom:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} (\phi_A(\mathbf{r}_1)\phi_B(\mathbf{r}_2) + \phi_B(\mathbf{r}_1)\phi_A(\mathbf{r}_2)), \quad (8.3)$$

where ϕ_A is an atomic orbital centered on nucleus A and similarly for B. The total density is just $n(\mathbf{r}) = n_A(\mathbf{r}) + n_B(\mathbf{r})$, where $n_I(\mathbf{r})$ is the hydrogen atom density centered on nucleus I. But note that the density remains unpolarized.

If we apply LSD to the exact density, we make a large error, because $E^{\text{LSD}}[n] = E^{\text{LDA}}[n_A] + E^{\text{LDA}}[n_B]$, and we saw in a previous chapter the huge error LDA makes for the H-atom, because it does not account for spin-polarization. We would much rather find $E^{\text{LSD}} = 2E^{\text{LSD}}(\text{H})$.

There is a way to do this, that has been well-known in quantum chemistry for years. If one allows a Hartree-Fock calculation to spontaneously break spin-symmetry, i.e., do not require the up-spin spatial orbital to be the same as that of the down-spin, then at a certain separation, called the Coulson-Fischer point, the unrestricted solution will have lower energy than the restricted one, and will yield the correct energy in the separated-atom limit, by producing two H atoms that have opposite spins. Thus we speak of RHF and UHF. The trouble with this is that the UHF solution is no longer a pure spin-eigenstate. Thus the symmetry dilemma is that an RHF calculation produces the correct spin symmetry with the wrong energy, while the UHF solution produces the right energy but with the wrong spin symmetry.

Kohn-Sham DFT calculations with approximate density functionals have a similar problem. The LSD calculation will spontaneously break symmetry at a Coulson-Fischer point (further than that of HF) to yield the appropriate energy. Now the dilemma is no longer the spin eigenvalue of the wavefunction, but rather the spin-densities themselves. In the unrestricted LDA calculation, which correctly dissociates to two LSD H atoms, the spin-densities are completely polarized, which is utterly incorrect.

8.4 Koopman's theorem

Since the large distance condition Eq. (3.42) is true for both the interacting wavefunction and an independent particle description, the following approximate theorem was first noted by Koopmans (who later won a Nobel prize in economics). In a Hartree-Fock calculation, if you ignore relaxation, meaning the change in the self-consistent potential, when an electron is removed from the system, you find

$$I^{\text{HF}} = E^{\text{HF}}(N-1) - E^{\text{HF}}(N) \approx -\epsilon_N \quad (8.4)$$

where ϵ_N is the eigenvalue of the highest occupied orbital.

Exercise 41 Koopman's theorem for 1d He

For the accurate HF 1-d He calculation, test Koopman's theorem.

But, in exact density functional theory, Koopman's theorem is *exact*. To see why, note that Eq. (3.42) is true *independent* of the strength of the interaction. Consider the coupling constant λ , keeping the density fixed. Since the density is fixed, its asymptotic decay is the same for *any* value of λ , i.e., the ionization potential is independent of λ . In particular, at $\lambda = 0$, it's just $-\epsilon^{\text{HOMO}}$, where we now refer to the HOMO of the KS potential. Thus

$$I = E(N-1) - E(N) = -\epsilon^{\text{HOMO}}. \quad (8.5)$$

We will see below that this condition is violated by all our approximate functionals.

Exercise 42 Asymptotic behavior of the density

From the information in this and earlier chapters, deduce the limiting values of the asymptotes on the right of Fig. 3.3.

8.5 Potentials

It is straightforward to argue for the exact asymptotic behaviour of the exchange-correlation potential for a Coulombic system. Consider first exchange. Far from the nucleus, and electron in an orbital should see an effective nuclear charge of $Z - (N - 1)$, the $N - 1$ because there are $N - 1$ electrons close to the nucleus. Since $v_{\text{ext}}(r) = -Z/r$, and at large distances $v_{\text{H}}(r) = N/r$, this implies $v_{\text{x}}(r) = -1/r$. Since this effect will occur in any wavefunction producing the exact density, this must also be true for $v_{\text{xc}}(r)$, so that the correlation contribution must decay more rapidly. In fact,

$$v_{\text{x}}(r) \rightarrow -1/r, \quad v_{\text{c}}(r) \rightarrow -\alpha(N - 1)/2r^4 \quad (r \rightarrow \infty) \quad (8.6)$$

where $\alpha(N - 1)$ is the polarizability of the $(N - 1)$ -electron species. The decay of the correlation potential is so rapid that it has only ever been clearly identified in an exact calculation for H^- .

Exercise 43 Asymptotic potentials

Derive the asymptotic condition on $v_{\text{x}}(r)$ from the exact decay of the density. How does $v_{\text{x}}^{\text{LDA}}(r)$ behave at large distances?

As mentioned earlier, LDA does not provide very realistic looking exchange-correlation potentials. Because the density decays exponentially in the tail region, so too will the LDA potential. In Fig. 8.2, we illustrate this effect. Of course, LDA also misses the shell structure between the 1s and 2s and 2p electrons, just as smooth approximations for T_{s} miss shell structure. This is partially explained by the above argument: the long-range decay of $v_{\text{x}}(r)$ is due to non-self-interaction in the exact theory, an effect missed by LDA. This has a strong effect on the HOMO orbital energy (and all those above it), as will be discussed in more detail below.

8.6 Derivative discontinuities

We can understand the apparent differences between LDA and exact potentials in much more detail. Consider what happens when two distinct subsystems are brought a large distance from each other. For example, take the H-He^+ case. At large distances, the interacting wavefunction for the two electrons should become two (unbalanced) Slater determinants, making up a Heitler-London type wavefunction, yielding a density that is

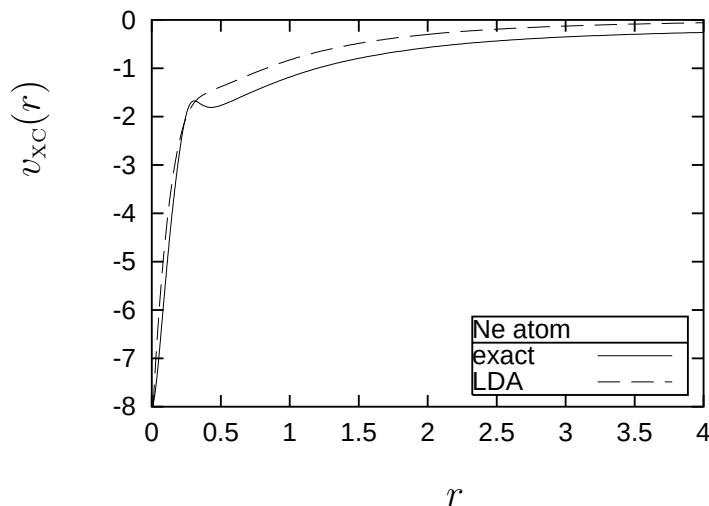


Figure 8.2: XC potential in the Ne atom, both exact and in LDA

the sum of the isolated atom densities, centered on each nucleus. In our world of 1-d illustrations, this will be

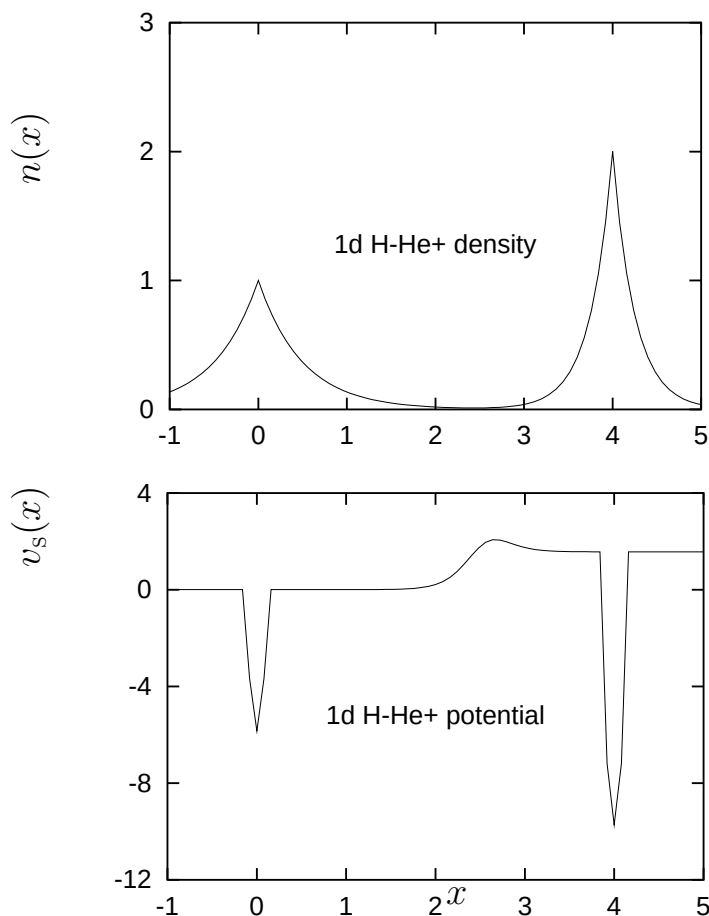
$$n(x) = \exp(-2|x|) + 2\exp(-4|x - L|) \quad (8.7)$$

where the H-atom is at 0 and the He ion is at L . For this two electron system, we find the molecular orbital as $\phi(x) = \sqrt{n(x)/2}$ and the Kohn-Sham potential by inversion. This is shown in Fig. 8.3, for $L = 4$. The apparent step in the potential between the atoms occurs where the dominant exponential decay changes. This is needed to ensure KS system produces two separate densities with separate decay constants. Elementary math then tells you that the step will be the size of the difference in ionization potentials between the two systems.

More generally, for e.g., NaCl being separated, the step must be the difference in I-E.A., where E.A. is the electron affinity. This is the energy cost of transferring an infinitesimal of charge from one system to another, and the KS potential must be constructed so that the molecule dissociates into neutral atoms. But the same reasoning can be applied to a single atom, in contact with a bath of electrons, eg a metal. One finds that the step in the potential induced by adding an infinitesimal of charge is I-EA.

But LDA is a smooth functional, with a smooth derivative. Thus its potential cannot discontinuously change when an infinitesimal of charge is added to the atom. So it will be in error about (I-EA)/2 for the neutral, and the reverse for the slightly negatively charged ion. Comparing the potentials for the Ne atom, we see in Fig. 8.4 how close the LDA potential is in the region around $r = 1$, relevant to the 2s and 2p electrons. However, it has been shifted down by -0.3, the LDA error in the HOMO orbital energy. Since Ne has zero electron affinity, this is close to (I-EA)/2 for this system, since I=0.8. This rationalizes one feature of the poor-looking potentials within LDA.

If the functional is generalized to include fractional particle numbers via ensemble

Figure 8.3: Density and Kohn-Sham potential for 1d H-He⁺.

DFT, these steps are due to discontinuities in the slope of the energy with respect to particle number at integer numbers of electrons. Hence the name.

8.7 Questions about some exact conditions not satisfied by LDA.

1. What kind of chemical systems will suffer from strong self-interaction error?
2. Which is better, to get the right energy and wrong symmetry, or vice versa?
3. Is Koopmans' theorem satisfied by LDA?
4. If one continues beyond $x = 5$ in Fig. 8.3, what happens?

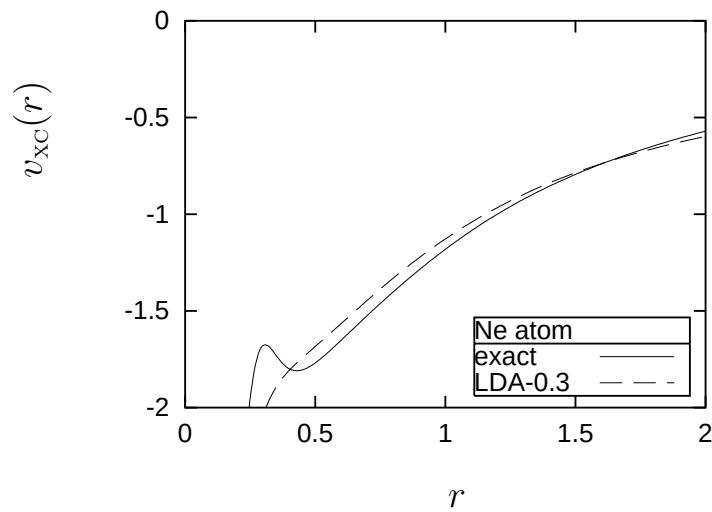


Figure 8.4: XC potential in the Ne atom, both exact and in LDA, in the valence region, but with LDA shifted down by -0.3.

Chapter 9

Exchange-correlation holes and the reliability of LDA

¹ In this chapter, we explore in depth the reliability of LSD. Although not accurate enough for thermochemistry, LSD has proven remarkably systematic in the errors that it makes. Improved functionals should incorporate this reliability. We will see that in fact, understanding the inherent reliability of LDA is the first step toward useful generalized gradient approximations.

9.1 Gradient expansion

Way back when, in the original Kohn-Sham paper, it was feared that LSD might not be too good an approximation (it turned out to be one of the most successful ever), and a simple suggestion was made to improve upon its accuracy. The idea was that, for any sufficiently slowly varying density, an expansion of a functional in gradients should be of ever increasing accuracy:

$$A^{\text{GEA}}[n] = \int d^3r \left(a(n(\mathbf{r})) + b(n(\mathbf{r}))|\nabla n|^2 + \dots \right) \quad (9.1)$$

Then, if LSD was moderately accurate for inhomogeneous systems, GEA, the gradient expansion approximation, should be more accurate. The form of these gradient corrections can be determined by scaling, while coefficients can be determined by several techniques.

For both T_s and E_x , defined on the Kohn-Sham wavefunction, the appropriate measure of the density gradient is given by

$$s(\mathbf{r}) = |\nabla n(\mathbf{r})|/(2k_F(\mathbf{r})n(\mathbf{r})) \quad (9.2)$$

This measures the gradient of the density on the length scale of the density itself, and has the important property that $s[n_\gamma](\mathbf{r}) = s[n](\gamma\mathbf{r})$, i.e., it is scale invariant. It often appears

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in the chemistry literature as $x = |\nabla n|/(n^{4/3})$, so that $x \approx 6s$. The gradient expansion of any functional with power-law scaling may be written as:

$$A^{\text{GEA}}[n] = \int d^3r a(n(\mathbf{r})) (1 + Cs^2(\mathbf{r})) \quad (9.3)$$

The coefficient may be determined by a semiclassical expansion of the Kohn-Sham density matrix, whose terms are equivalent to a gradient expansion. One finds

$$C_s = 5/27, \quad C_x = 10/81 \quad (9.4)$$

(In fact, a naive zero-temperature expansion gives $C_x = 7/81$, but a more sophisticated calculation gives the accepted answer above). The gradient correction generally improves both the non-interacting kinetic energy and the exchange energy of atoms. The improvement in the exchange energy is to reduce the error by about a factor of 2.

Exercise 44 *For the H-atom, calculate the gradient corrections to the kinetic and exchange energies. (Don't forget to spin-scale).*

For correlation, the procedure remains as simple in principle, but more difficult in practice. Now, there are non-trivial density- and spin- dependences, and the terms are much harder to calculate in perturbation theory. In the high-density limit, the result may be written as

$$\Delta E_c^{\text{GEA}} = \frac{2}{3\pi^2} \int d^3r n(\mathbf{r}) \phi(\zeta(\mathbf{r})) t^2(\mathbf{r}). \quad (9.5)$$

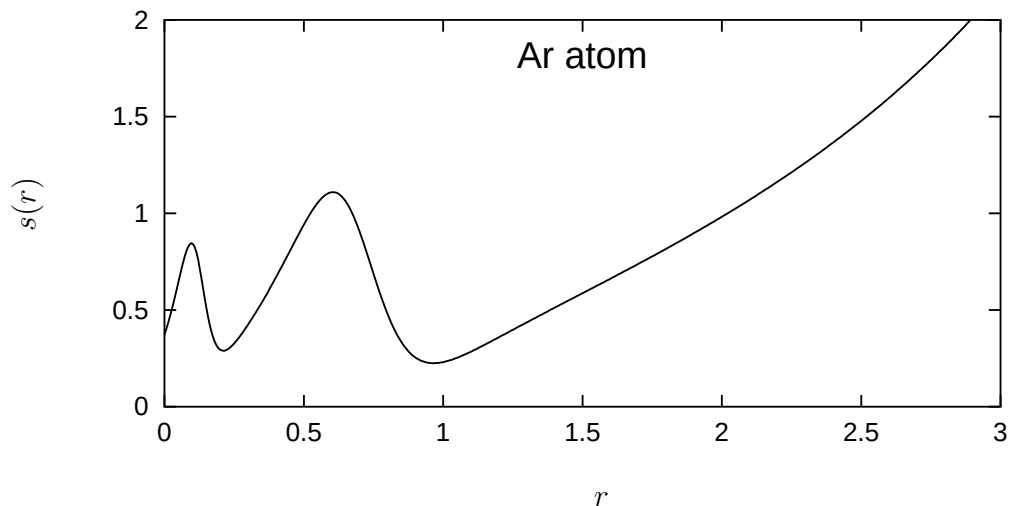
Here $t = |\nabla n|/(2k_s n)$, where $k_s = \sqrt{4k_F/\pi}$ is the Thomas-Fermi screening length, the natural wavevector scale for correlations in a uniform system. The spin-polarization factor is $\phi(\zeta) = ((1+\zeta)^{2/3} + (1-\zeta)^{2/3})/2$. This correction behaves poorly for atoms, being positive and sometimes larger in magnitude than the LSD correlation energy, leading to positive correlation energies!

Exercise 45 *Calculate the GEA correction to the H atom energy, and show how ΔE_c^{GEA} scales in the high-density limit.*

9.2 Gradient analysis

Having seen in intimate detail which r_s values are important to which electrons in Fig. reff:rsAr, we next consider reduced gradients. Fig. 9.1 is a picture of $s(r)$ for the Ar atom, showing how s changes from shell to shell. Note first that, at the nucleus, s has a finite moderate value. Even though the density is large in this region, the reduced gradient is reasonable.

Exercise 46 *Show that at the origin of a hydrogen atom, $s(0) = 0.38$, and argue that this value won't change much for any atom.*

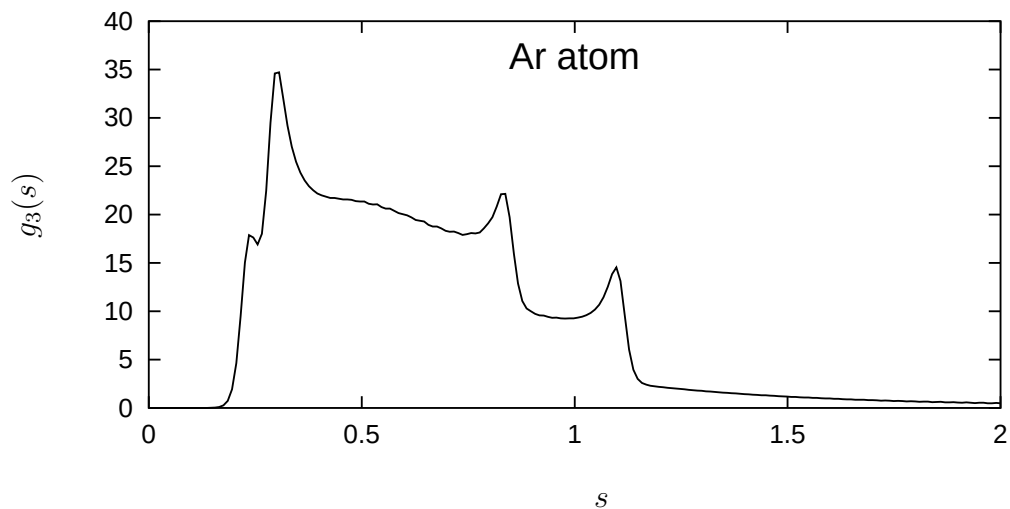
Figure 9.1: $s(r)$ in Ar atom.

For any given shell, e.g. the core electrons, s grows exponentially. When another shell begins to appear, there exists a turnover region, in which the gradient drops rapidly, before being dominated once again by the decay of the new shell. We call these intershell regions.

We define a density of reduced gradients, analogous to our density of r_s 's:

$$g_3(s) = \int d^3r \, n(\mathbf{r}) \, \delta(s - s(\mathbf{r})), \quad (9.6)$$

also normalized to N , and plotted for the Ar atom in Fig. 9.2. Note there is *no* contribu-

Figure 9.2: $g_3(s)$ in Ar atom.

tion to atoms (or molecules) from regions of $s = 0$. Note also that almost all the density has reduced gradients less than about 1.2, with a long tail stretching out of larger s .

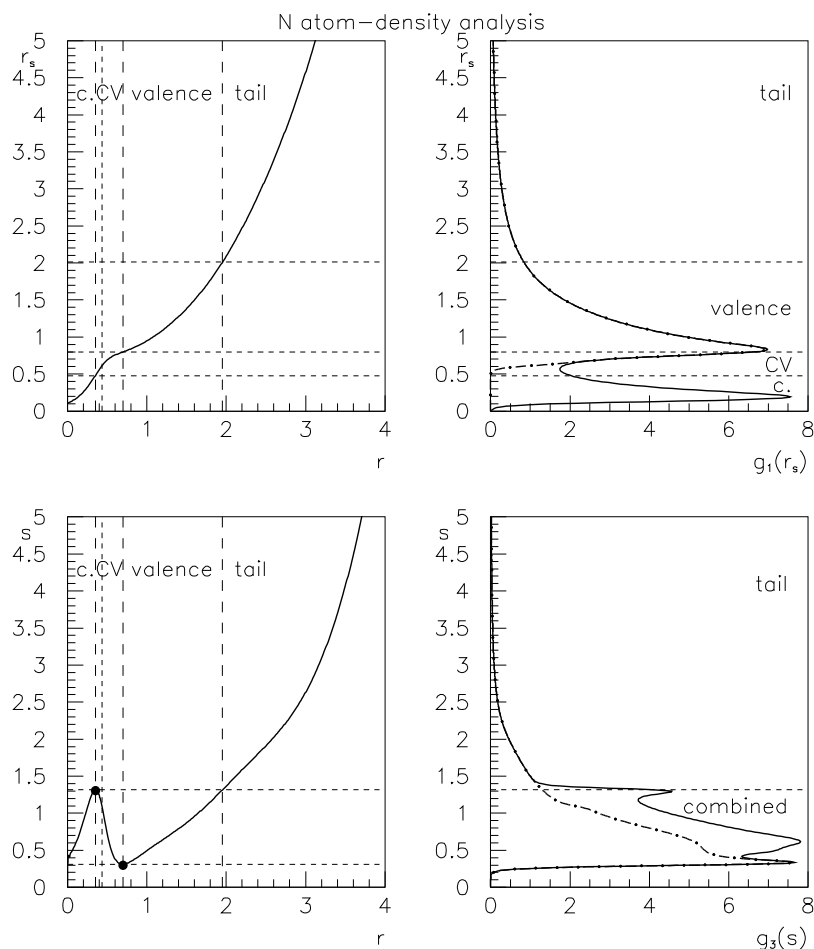


Figure 9.3: Distribution of densities and gradients in the N atom.

We now divide space around atoms into spheres. We will (somewhat arbitrarily) denote the valence region as all r values beyond the last minimum in $s(r)$, containing 6.91 electrons in Ar. We will denote the region of all r smaller than the position of the last peak in s as being the core region (9.34 electrons). The last region in which s decreases with r is denoted the core-valence region, in which the transition occurs (1.75 electrons). We further denote the tail region as being that part of the valence region where s is greater than its maximum in the core (1.54 electrons).

To see how big s can be in a typical system that undergoes chemical reactions, consider Fig. 9.3. On the left is plotted values of r_s (top) and of s (bottom) as a function of r in an N atom. Then on the right are plotted the distribution of values (turned sideways). We see that the core electrons have $r_s \leq 0.5$, while the valence electrons have $0.5 \leq r_s \leq 2$. The s -values are more complex, since they are similar in both the core and valence regions.

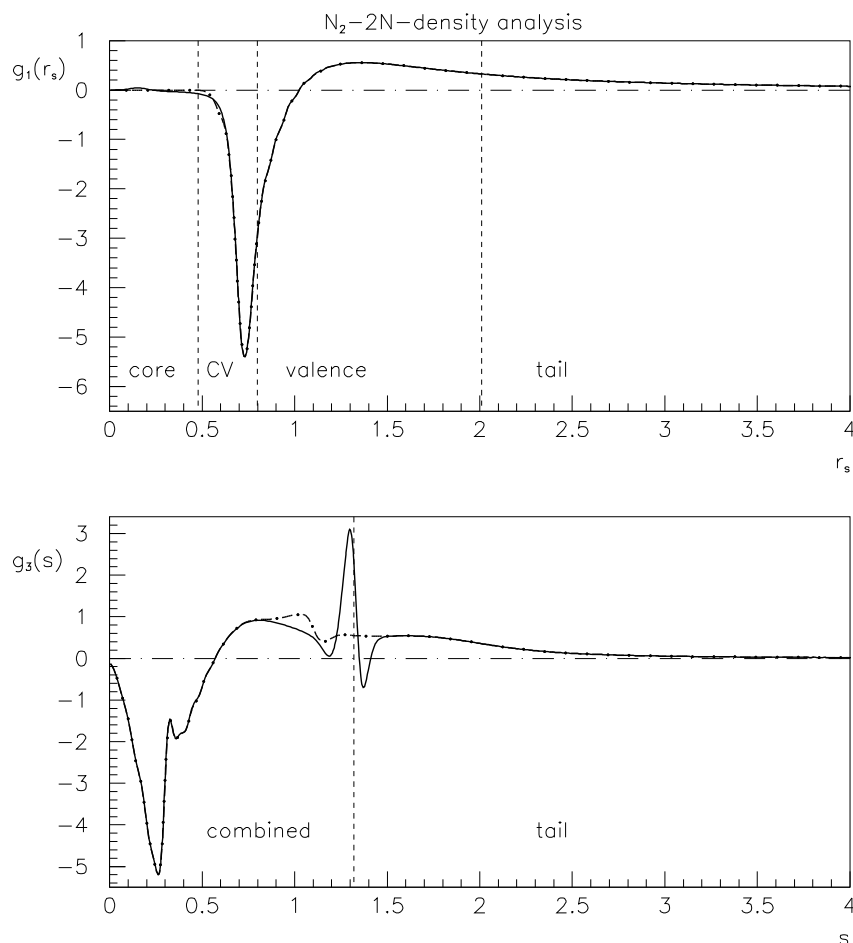


Figure 9.4: Differences in distribution of densities and gradients upon atomization of the N_2 molecule.

We see that almost all the density has $0.2 \leq s \leq 1.5$. Because s is not monotonic, many regions in space can contribute to $g_3(s)$ for a given s value. To better distinguish them, one can perform a pseudopotential calculation, that replaces the core electrons by an effective potential designed only to reproduce the correct valence density. This is marked in the two right-hand panels by a long-dashed line. In the $g_3(r_s)$ figure, we see indeed that the pseudopotential is missing precisely the inner core peak, while in the $g(s)$ figure, we see the contribution of the valence electrons alone to the peak from the combined core-valence region.

We may use the s curve to make more precise (but arbitrary) definitions of the various shells. Up to the first maximum in s we call the core. The small region where s drops rapidly is called the core-valence intershell region. The region in which s grows again, but remains below its previous maximum, we call the valence region. The remainder is denoted

the tail. We make these regions by vertical dashed lines, which have been extended to the upper r_s curve. Because that curve is monotonic, we can draw horizontal lines to meet the vertical lines along the curve, and thus divide the $g(r_s)$ curve into corresponding regions of space.

But we are more interested in atomization energies than atomic energies. In the case of a molecule, there is no simple monotonic function, but one can easily extract the densities of variables. Having done this for the molecule, we can make a plot of the differences between (twice) the atomic curves and the molecular curve. Now the curves are both positive and negative. We see immediately that the core does not change on atomization of the molecule, and so is irrelevant to the atomization energy. Interestingly, it is also clear that it is not only the valence electrons ($r_s > 0.8$) that contribute, but also the core-valence region, which include r_s values down to 0.5. Finally, note that the r_s values contributing to this energy also extend to higher r_s regions.

To summarize what we have learned from the gradient analysis:

- Note again that nowhere in either the N or Ar atoms (or any other atom) has $s \ll 1$, the naive requirement for the validity of LSD. Real systems are not slowly-varying. Even for molecules and solids, only a very small contribution to the energy comes from regions with $s < 0.1$.
- A generalized gradient approximation, that depends also on values of s , need only do well for $s \leq 1.5$ to reproduce the energy of the N atom. To get most chemical reactions right, it need do well only for $s \leq 3$.

We end by noting that while this analysis can tell us which values of r_s and s are relevant to real systems, it does *not* tell us how to improve on LSD. To demonstrate this, in Fig. 9.5, we plot the exchange energy per electron in the He atom. One clearly sees

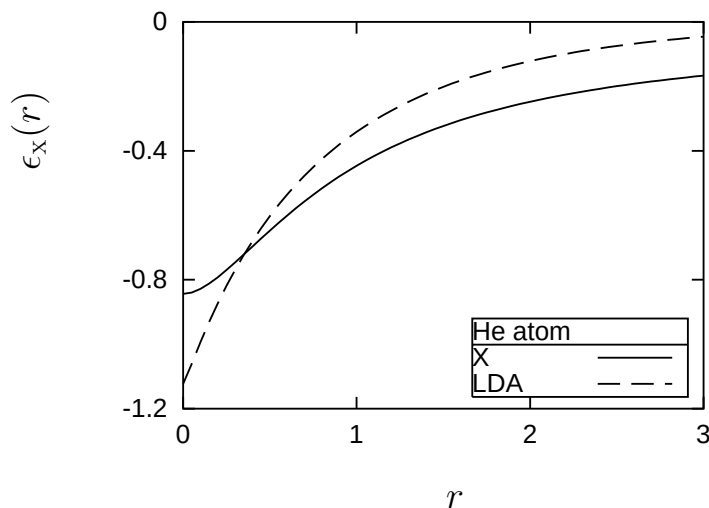


Figure 9.5: Exchange energy per electron in the He atom, both exactly and in LDA. The nucleus is at $r = 0$.

an apparent cancellation of errors throughout the system, i.e., LDA is *not* describing this quantity well at each point in the system, but it does a good job for its integral. As we will show below, a pointwise analysis of energy densities turns out to be, well, somewhat pointless...

9.3 Density matrices and holes

We now dig deeper, to understand better why LSD works so reliably, even for highly inhomogeneous systems. We must first return to the many-body wavefunction. We define the following (first-order) density matrix:

$$\gamma(x, x') = N \int dx_2 \dots \int dx_N \Psi^*(x, x_2, \dots, x_N) \Psi(x', x_2, \dots, x_N) \quad (9.7)$$

The diagonal elements of this density matrix are just the spin-densities:

$$\gamma(x, x) = n(x) \quad (9.8)$$

and the exact kinetic energy can be extracted from the spin-summed (a.k.a reduced) density matrix:

$$\gamma(\mathbf{r}, \mathbf{r}') = \sum_{\sigma\sigma'} \gamma(\mathbf{r}\sigma, \mathbf{r}'\sigma') \quad (9.9)$$

and

$$T = -\frac{1}{2} \int d^3r \nabla^2 \gamma(\mathbf{r}, \mathbf{r}')|_{\mathbf{r}=\mathbf{r}'} \quad (9.10)$$

Note that, although $\gamma(x, x')$ is a one-body property, only its diagonal elements are determined by the density. For example, we know that γ_s , the density matrix in the Kohn-Sham system, differs from the true density matrix, since the true kinetic energy differs from the non-interacting kinetic energy:

$$T_C = -\frac{1}{2} \int d^3r \nabla^2 (\gamma(\mathbf{r}, \mathbf{r}') - \gamma_s(\mathbf{r}, \mathbf{r}'))|_{\mathbf{r}=\mathbf{r}'} \quad (9.11)$$

For a single Slater determinant, we have the following simple result:

$$\gamma_s(x, x') = \delta_{\sigma\sigma'} \sum_{i=1}^{N_\sigma} \phi_{i\sigma}^*(\mathbf{r}) \phi_{i\sigma}(\mathbf{r}') \quad (9.12)$$

where $\phi_{i\sigma}(\mathbf{r})$ is the i -th Kohn-Sham orbital of spin σ . This is diagonal in spin.

Exercise 47 For same-spin electrons in a large box (from 0 to L , where $L \rightarrow \infty$) in one-dimension, show that

$$\gamma_s(x, x') = \frac{k_F}{\pi} \left(\frac{\sin(k_F(x - x'))}{k_F(x - x')} - \frac{\sin(k_F(x + x'))}{k_F(x + x')} \right). \quad (9.13)$$

Prove this density matrix has the right density, and extract $t_s(x)$ from it.

We will, however, focus more on the potential energy, since that appears directly in the usual adiabatic connection formula. To this end, we define the pair density:

$$P(x, x') = N(N-1) \int dx_3 \dots \int dx_N |\Psi(x, x', x_3, \dots, x_N)|^2 \quad (9.14)$$

which is also known as the (diagonal) second-order density matrix. This quantity has an important physical interpretation: $P(\mathbf{r}\sigma, \mathbf{r}'\sigma')d^3rd^3r'$ is the probability of finding an electron of spin σ in d^3r around $\mathbf{r}$, and a second electron of spin σ' in d^3r' around $\mathbf{r}'$. Thus it contains information on the *correlations* among the electrons. To see this, we may write:

$$P(x, x')d^3rd^3r' = \{n(x)d^3r\} \{n_2(x, x')d^3r'\} \quad (9.15)$$

where $n_2(x, x')d^3r'$ is the *conditional* probability of finding the second electron of spin σ' in d^3r' around $\mathbf{r}'$, given that an electron of spin σ has already been found in d^3r around $\mathbf{r}$. Now, if the finding of the second electron were completely independent of the first event, then $n_2(x, x') = n(x')$. This can *never* be true for any wavefunction, since, by definition:

$$\int dx' P(x, x') = (N-1) n(x) \quad (9.16)$$

implying:

$$\int dx' n_2(x, x') = N-1, \quad (9.17)$$

i.e., the fact that we have found one electron already, implies that the remaining conditional probability density integrates up to *one less* number of electrons.

Exercise 48 *Show that*

$$\int dx' P(x, x') = (N-1) n(x) \quad (9.18)$$

and state this result in words. What is the pair density of a one-electron system? Deduce what you can about the parallel and antiparallel pair density of a spin-unpolarized two electron system, like the He atom.

Why is this an important quantity? Just as the kinetic energy can be extracted from the first-order density matrix, the potential energy of an interacting electronic system is a two-body operator, and is known once the pair density is known:

$$V_{ee} = \frac{1}{2} \int dx \int dx' P(x, x') / |\mathbf{r} - \mathbf{r}'| \quad (9.19)$$

Although it can be very interesting to separate out the parallel and antiparallel spin contributions to the pair density, we won't do that here, since the Coulomb repulsion does not. The reduced pair density is the spin-summed pair density:

$$P(\mathbf{r}, \mathbf{r}') = \sum_{\sigma\sigma'} P(\mathbf{r}\sigma, \mathbf{r}'\sigma'), \quad (9.20)$$

and is often called simply the pair density. Then

$$V_{ee} = \frac{1}{2} \int d^3r \int d^3r' \frac{P(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (9.21)$$

As we have seen, a large chunk of V_{ee} is simply the Hartree electrostatic energy U , and since this is an explicit density functional, does not need to be approximated in a Kohn-Sham calculation. Thus it is convenient to subtract this off. We define the (potential) exchange-correlation hole density around an electron at $\mathbf{r}$ of spin σ :

$$P(x, x') = n(x) (n(x') + n_{xc}(x, x')). \quad (9.22)$$

The hole is usually (but not always) negative, and integrates to exactly -1 :

$$\int dx' n_{xc}(x, x') = -1 \quad (9.23)$$

Since the pair density can never be negative,

$$n_{xc}(x, x') \geq -n(x'). \quad (9.24)$$

This is not a very strong restriction, especially for many electrons. Again, while the spin-decomposition of the hole is interesting, our energies depend only on the spin-sum, which is less trivial for the hole:

$$n_{xc}(\mathbf{r}, \mathbf{r}') = \left(\sum_{\sigma\sigma'} n(x) n_{xc}(x, x') \right) / n(\mathbf{r}). \quad (9.25)$$

The pair density is a symmetrical function of $\mathbf{r}$ and $\mathbf{r}'$:

$$P(\mathbf{r}', \mathbf{r}) = P(\mathbf{r}, \mathbf{r}'), \quad (9.26)$$

but the hole is not. It is often useful to define $\mathbf{u} = \mathbf{r}' - \mathbf{r}$ as the distance away from the electron, and consider the hole as function of $\mathbf{r}$ and $\mathbf{u}$. These ideas are illustrated in Fig. (9.6). It is best to think of the hole as a function of $u = x' - x$, i.e., distance from the electron point. The hole is often (but not always) deepest at the electron point, and decays rapidly with distance, as the electrons avoid the electron at x . The product of densities in $P(\mathbf{r}, \mathbf{r}')$ gives rise to U , the Hartree energy, while

$$U_{xc} = \int d^3r n(\mathbf{r}) \int d^3u \frac{n_{xc}(\mathbf{r}, \mathbf{u})}{2u}. \quad (9.27)$$

Thus we may say, in a wavefunction interpretation of density functional theory, the exchange-correlation energy is simply the Coulomb interaction between the charge density and its surrounding exchange-correlation hole.

The exchange hole is a special case, and arises from the Kohn-Sham wavefunction. For a single Slater determinant, one can show

$$P_x(x, x') = \sum_{i=1}^{N_\sigma} \sum_{j=1}^{N_{\sigma'}} \phi_{i\sigma}^*(\mathbf{r}) \phi_{j\sigma'}^*(\mathbf{r}') (\phi_{i\sigma}(\mathbf{r}) \phi_{j\sigma'}(\mathbf{r}') - \phi_{i\sigma}(\mathbf{r}') \phi_{j\sigma'}(\mathbf{r})) \quad (9.28)$$

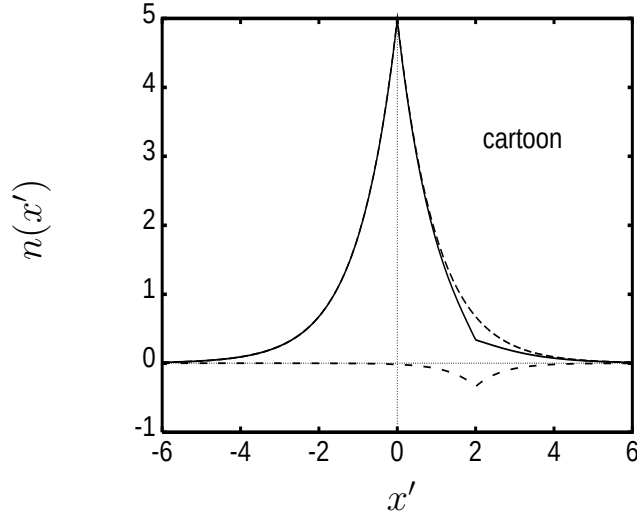


Figure 9.6: Cartoon of hole in one-dimensional exponential density. Plotted are the actual density $n(x')$ (long dashes), the conditional density $n_2(x=2, x')$ (solid line), and their difference, the hole density, $n_{xc}(x=2, x')$ (dashed line).

The first (direct) term clearly yields simply the product of the spin-densities, $n(x)n(x')$, while the second (exchange) term can be expressed in terms of the density matrix:

$$P_x(x, x') = n(x)n(x') - |\gamma_s(x, x')|^2 \quad (9.29)$$

yielding

$$n_x(x, x') = -|\gamma_s(x, x')|^2 / n(x). \quad (9.30)$$

This shows that the exchange hole is diagonal in spin (i.e., only like-spins exchange) and is everywhere negative. Since exchange arises from a wavefunction, it satisfies the sum-rule, so that

$$\int d^3u \, n_x(\mathbf{r}, \mathbf{u}) = -1 \quad (9.31)$$

The exchange hole gives rise to the exchange energy:

$$E_x = \frac{1}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n_x(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (9.32)$$

Exercise 49 Spin-scaling the hole

Deduce the spin-scaling relation for the exchange hole.

Exercise 50 Holes for one-electron systems

For the H atom (in 3d), plot $P(\mathbf{r}, \mathbf{r}')$, $n_2(\mathbf{r}, \mathbf{r}')$ and $n_x(\mathbf{r}, \mathbf{r}')$ for several values of $\mathbf{r}$ as a function of $\mathbf{r}'$, keeping $\mathbf{r}'$ parallel to $\mathbf{r}$.

The correlation hole is everything not in the exchange hole. Since the exchange hole satisfies the sum-rule, the correlation hole must integrate to zero:

$$\int d^3u \, n_c(\mathbf{r}, \mathbf{u}) = 0. \quad (9.33)$$

This means the correlation hole has both positive and negative parts, and occasionally the sum of exchange and correlation can be positive. It also has a universal cusp at $u = 0$, due to the singularity in the electron-electron repulsion there.

An alternative way of representing the same information that is often useful is the pair-correlation function:

$$g(x, x') = P(x, x') / (n(x)n(x')) \quad (9.34)$$

This pair-correlation function contains the same information as the hole, but can make some results easier to state. For example, at small separations, the Coulomb interaction between the electrons dominates, leading to the electron-electron cusp in the wavefunction:

$$dg^{\text{sph.av.}}(\mathbf{r}, u)/du|_{u=0} = g^{\text{sph.av.}}(\mathbf{r}, u=0), \quad (9.35)$$

where the superscript denotes a spherical average in $\mathbf{u}$. Similarly, at large separations, $g \rightarrow 1$ as $u \rightarrow \infty$ in extended systems, due to the screening effect, but not so for finite systems. Furthermore, the approach to unity differs between metals and insulators.

9.4 An illustration of holes: Hooke's atom

A useful and interesting alternative external potential to the Coulomb attraction of the nucleus for electrons is the harmonic potential. Hooke's atom consists of two electrons in a harmonic well of force constant k , with a Coulomb repulsion. It is useful because it is exactly solvable, so that many ideas can be tested, and also (more importantly), many general concepts can be illustrated.

Exercise 51 Hooke's atom: Approximate HF

Repeat the approximate HF calculation of chapter 3 on Hooke's atom, using appropriate orbitals. Make a definite statement about the ground-state and HF energies.

Exercise 52 Hooke's atom: Separation of variables

Show that, for two electrons in external potential $v_{\text{ext}}(r) = kr^2/2$, and with Coulomb interaction, the ground-state wavefunction may be written as

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Phi(R)\phi(u), \quad (9.36)$$

where $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$, $\mathbf{u} = \mathbf{r}_2 - \mathbf{r}_1$, $\Phi(R)$ is the ground-state orbital of a 3-d harmonic oscillator of mass 2, and $\phi(u)$ satisfies

$$\left\{ -\nabla_u^2 + \frac{ku^2}{4} + \frac{1}{u} \right\} \phi(u) = \epsilon_u \phi(u) \quad (9.37)$$

Exercise 53 Hooke's atom exactly

Show that the function $\phi(u) = C(1 + u/2) \exp(-u^2/4)$ satisfies the Hooke's atom equation (9.37) with $k = 1/4$, and find the exact ground-state energy. How big was your error in your estimated energy above? Make a rigorous statement about the correlation energy.

Exercise 54 Hooke's atom: Exchange and correlation holes

Use the exact wavefunction for Hooke's atom at $k = 1/4$ to plot both $n_x(\mathbf{r}, \mathbf{u})$ and $n_c(\mathbf{r}, \mathbf{u})$ for $r = 0$ and 1, with $\mathbf{u}$ parallel to $\mathbf{r}$. The exact density is:

$$n(r) = \sqrt{2}C^2 \exp(-r^2/2)/r \times \left\{ 7r + r^3 + 8r \exp(-r^2/2)/\sqrt{2\pi} + 4(1 + r^2)\text{erf}(r/\sqrt{2}) \right\} \quad (9.38)$$

where the error function is

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x dy \exp(-y^2) \quad (9.39)$$

and $C^{-1} = 2\sqrt{5\pi + 8\sqrt{\pi}}$

Exercise 55 Hooke's atom: Electron-electron cusp

Repeat the above exercise for the pair-correlation function, both exchange and exchange-correlation. Where is the electron-electron cusp? What happens as $u \rightarrow \infty$?

9.5 Transferability of holes

The pair density looks very different from one system to the next. But let us consider two totally different systems: the 1-d H-atom and the (same-spin) 1-d uniform electron gas. For any one-electron system, the pair density vanishes, so

$$n_x(\mathbf{r}, \mathbf{r}') = -n(\mathbf{r}') \quad (N = 1). \quad (9.40)$$

For our 1d H atom, this is just $n(x + u)$, where $n(x) = \exp(-2|x|)$, and is given by the solid curve in Fig. 9.7, with $x = 0$. On the other hand, we can deduce the exchange hole

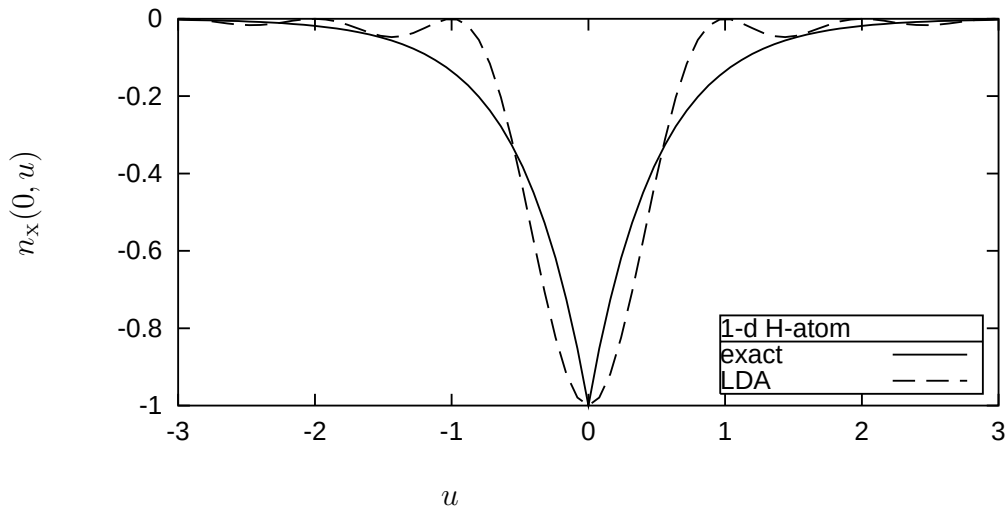


Figure 9.7: Exchange hole at center of one-dimensional H-atom, both exactly and in LDA.

for the uniform gas from the bulk value of the first-order density matrix. From Eq.(9.13), taking x, x' to be large, we see that the density matrix becomes, in the bulk,

$$\gamma_s^{\text{unif}}(u) = n \sin(k_F u) / (k_F u) \quad (9.41)$$

leading to

$$n_x(u) = -n \sin^2(k_F u) / (k_F u)^2 \quad (9.42)$$

These depend only on the separation between points, as the density is constant in the system. They also are symmetric in u , as there cannot be any preferred direction. This hole is also plotted in Fig. 9.7, for a density of $n = 1$, the density at the origin in the 1-d H-atom.

Comparison of the uniform gas hole and the H-atom hole is instructive. They are remarkably similar, even though their pair densities are utterly different. If the electron-electron repulsion is taken as $\delta(u)$, $U = 1/8$ for the 1d H-atom, while U diverges for the uniform gas. Why are they so similar? Because they are both holes of some quantum mechanical system. So both holes are normalized, and integrate to -1. They are also equal at the ontop value, $u = 0$.

Exercise 56 Ontop exchange hole *Show that the ontop exchange hole is a local-spin density functional, and give an expression for it.*

Why is this important? We may think of the local approximation as an approximation to the hole, in the following way:

$$n_x^{\text{LDA}}(x, x+u) = n_x^{\text{unif}}(n(x); u), \quad (9.43)$$

i.e., the local approximation to the hole at any point is the hole of a uniform electron gas, whose density is the density at the electron point. Fig 9.7 suggests this will be a pretty good approximation. Then the energy per electron due to the hole is just

$$\epsilon_x(x) = \int_{-\infty}^{\infty} du v_{ee}(u) n_x(x, x+u), \quad (9.44)$$

with

$$E_x = \int_{-\infty}^{\infty} dx n(x) \epsilon_x(x). \quad (9.45)$$

Since, for the uniform gas,

$$\epsilon_x^{\text{unif}}(n) = \int_{-\infty}^{\infty} du v_{ee}(u) n_x^{\text{unif}}(n; u), \quad (9.46)$$

we may consider $E_x^{\text{LDA}}[n]$ as arising from a local approximation to the hole at x . Thus, the general similarities tell us that LDA should usually be in the ball park. In fact, if $v_{ee}(u) = -\delta(u)$ as we have used in the past, and since the exact ontop hole is just $-n(x)$, then LDA would be exact for X in that 1d world. But since the real Coulomb interaction in 3d is not a contact interaction, we will imagine a 1d world in which the repulsion

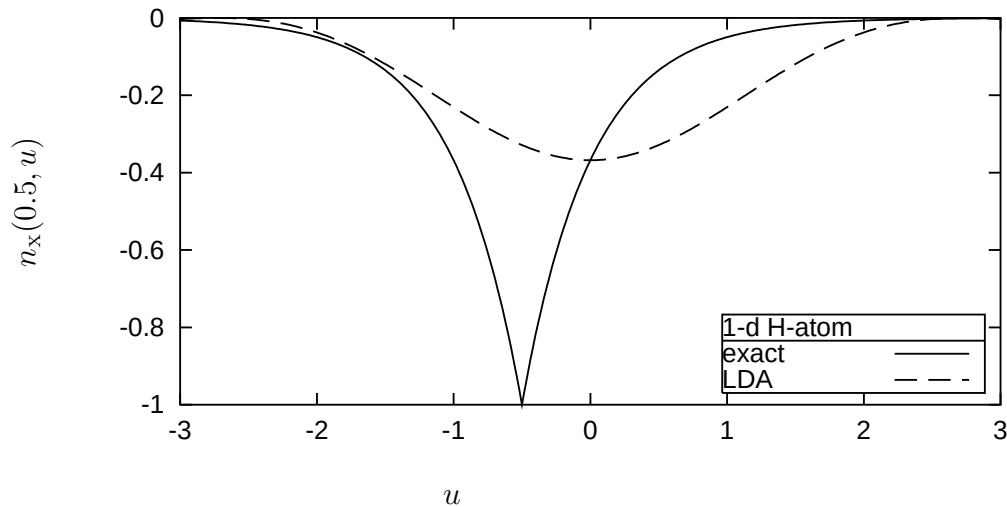


Figure 9.8: Exchange hole at $x = 0.5$ of one-dimensional H-atom, both exactly and in LDA.

is $\exp(-2|u|)$. Then, because the overall hole shapes are similar, we find $\epsilon(0) = -0.5$ exactly, and $= -0.562$ in LDA.

We have shown above how to understand qualitatively why LDA would give results in the right ball-park. But can we use this simple picture to understand *quantitatively* the LDA exchange? If we calculate the exchange energy per electron everywhere in the system, we get Fig. 9.9. This figure resembles that of the real He atom given earlier.

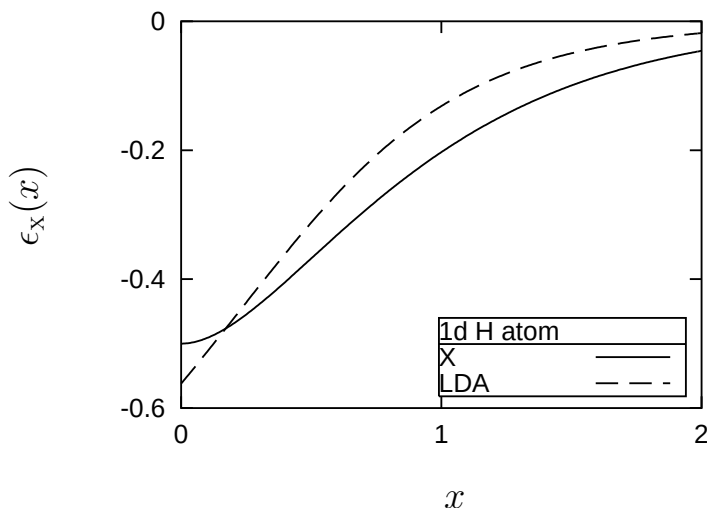


Figure 9.9: Exchange energy per electron in the one-dimensional H-atom, both exactly and in LDA, for repulsion $\exp(-2|u|)$.

Looked at more closely, our naive hopes are dashed. In fact, our $x = 0$ case is more an anomaly than typical. We find, for our exponential repulsion, $E_x = -0.351$ in LDA, and -0.375 exactly, i.e., the usual 10% underestimate in magnitude by LDA. But at $x = 0$, the LDA *overestimates* the contribution, while for large x , it underestimates it.

At this point, we do well to notice the difference in detail between the two holes. The exact H-atom hole contains a cusp at $u = 0$, missing from the uniform gas hole. This causes it to deviate quickly from the uniform gas hole near $u = 0$. At large distances, the H-atom hole decays exponentially, because the density does, while the uniform gas hole decays slowly, being a power law times an oscillation. These oscillations are the same Friedel oscillations we saw in the surface problem. For an integral weighted $\exp(-2|u|)$, the rapid decay of the exact hole leads to a smaller energy density than LDA.

Now watch what happens when we move the hole point off the origin. In Fig. 9.8, we plot the two holes at $x = 0.5$. The H-atom hole is said to be *static*, since it does not change position with x . By plotting it as a function of u , there is a simple shift of origin. The hole remains centered on the nucleus, which is now at $u = -0.5$. On the other hand, we will see that for most many electron systems, the hole is typically quite dynamic, and follows the position where the first electron was found. This is entirely true in the uniform gas, whose hole is always symmetrically placed around the electron point, as seen in this figure. Note that, although it is still true that both holes are normalized to -1 , and that the ontop values still agree, the strong difference in shape leads to more different values of $\epsilon(x)$ (-0.312 in LDA, and -0.368 exactly). In Fig. 9.9, we plot the resulting exchange energy/electron throughout the atom. The LDA curve only loosely resembles the exact curve. Near the nucleus it has a cusp, and overestimates $\epsilon_x(x)$. As x gets even larger, $n(x)$ decays exponentially, so that the LDA hole becomes very diffuse, since its length scale is determined by $1/k_F$, where $k_F = \pi n$, while the exact hole never changes, but simply moves further away from the electron position. large x . When weighted by the electron density, to deduce the contribution to the exchange energy, there is a large cancellation of errors between the region near the nucleus and far away. (To see the similarities with real systems, compare this figure with that of Fig. 9.5).

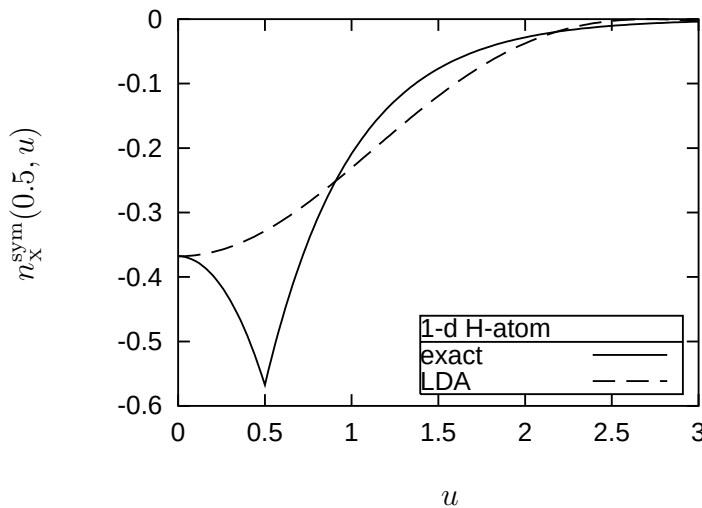


Figure 9.10: Symmetrized exchange hole at $x = 0.5$ of one-dimensional H-atom, both exactly and in LDA.

But, while all the details of the hole are clearly not well-approximated in LDA, espe-

cially as we move around in a finite system, we now show that the important averages over the hole *are*. To begin with, both positive and negative values contribute equally, so we may write:

$$E_x = \int_{-\infty}^{\infty} dx n(x) \int_0^{\infty} du n_x^{\text{sym}}(x, u), \quad (9.47)$$

where

$$n_x^{\text{sym}}(x, u) = \frac{1}{2} (n_x(x, u) + n_x(x, -u)) \quad (9.48)$$

This symmetrizing has no effect on the LDA hole, since it is already symmetric, but Fig. ?? shows that it improves the agreement with the exact case: both holes are now parabolic around $u = 0$, and the maximum deviation is much smaller. However, the cusp at the nucleus is clearly missing from the LDA hole, and still shows up in the exact hole.

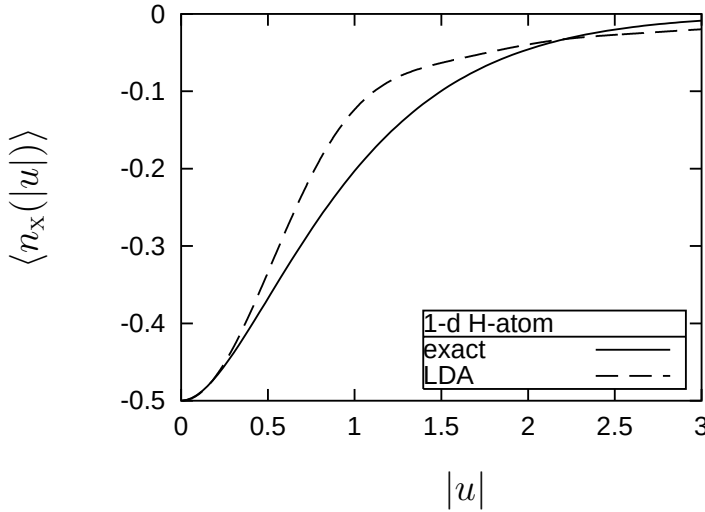


Figure 9.11: System-averaged symmetrized exchange hole of one-dimensional H-atom, both exactly and in LDA.

Our last and most important step is to point out that, in fact, it is the system-averaged symmetrized hole that appears in E_x , i.e.,

$$\langle n_x(u) \rangle = \int_{-\infty}^{\infty} dx n(x) n_x^{\text{sym}}(x; u) \quad (9.49)$$

where now u always taken to be positive, since

$$E_x = \int_0^{\infty} du v_{ee}(u) \langle n_x(u) \rangle \quad (9.50)$$

The system-averaged symmetrized hole is extremely well-approximated by LDA. Note how no cusps remain in the exact hole, because of the system-averaging. Note how both rise smoothly from the same ontop value. Note how LDA underestimates the magnitude at moderate u , which leads to the characteristic underestimate of LDA exchange energies. Finally, multiplying by $v_{ee} = \exp(-2|u|)$, we find Fig. 9.12. Now the 10% underestimate

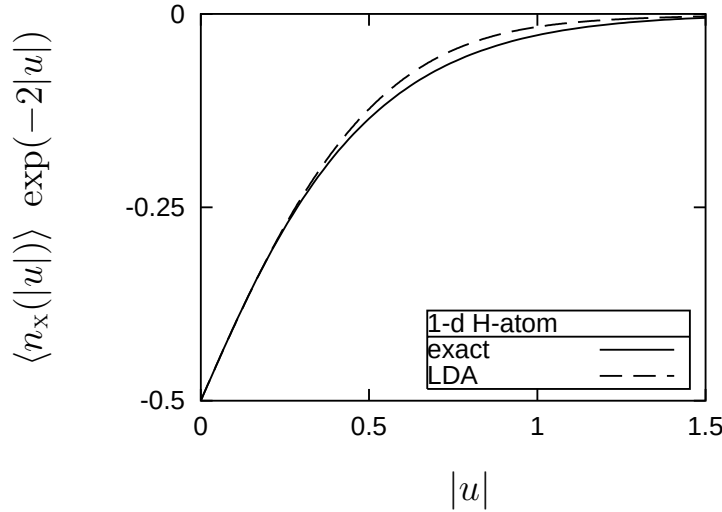


Figure 9.12: System-averaged symmetrized exchange hole of one-dimensional H-atom, both exactly and in LDA, weighted by $\exp(-2|u|)$.

is clearly seen, with no cancellation of errors throughout the curve.

We can understand this as follows. For small u , a local approximation can be very accurate, as the density cannot be very different at $x + u$ from its value at x . But as u increases, the density at $x + u$ could differ greatly from that at x , especially in a highly inhomogeneous system. So the short-ranged hole is well-approximated, but the long-range is not. In fact, for large u , the oscillating power-law LDA behavior is completely different from the exponentially decaying exact behavior:

Exercise 57 *Show that the exact system-averaged symmetrized hole in the 1-d H atom is:*

$$\langle n_x(u) \rangle = -\exp(-2u) (1 + 2u), \quad (= f(\pi u) \text{ LSD}), \quad (9.51)$$

where

$$f(z) = -\frac{2}{z^2} \int_0^z dz' \sin^2(z')/z'. \quad (9.52)$$

But the constraint of the sum-rule and the wonders of system- and spherical- (in the 3d case) averaging lead to a very controlled extrapolation at large u . This is the true explanation of LDA's success. Notice also that this explanation requires that uniform gas values be used: Nothing else implicitly contains the information about the hole.

9.6 Old faithful

We are now in a position to understand why LSD is such a reliable approximation. While it may not be accurate enough for most quantum chemical purposes, the errors it makes are very systematic, and rarely very large.

We begin from the ansatz that LSD is a model for the exchange-correlation hole, not just the energy density. We denote this hole as $n_{\text{xc}}^{\text{unif}}(r_s, \zeta; u)$, being the hole as a function of separation u of a uniform gas of density $(4\pi r_s^3/3)^{-1}$ and relative spin-polarization ζ . Then, by applying the technology of the previous section to the uniform gas, we know the potential exchange-correlation energy density is given in terms of this hole:

$$u_{\text{xc}}^{\text{unif}}(r_s, \zeta) = 2\pi \int_0^\infty du u n_{\text{xc}}^{\text{unif}}(r_s, \zeta; u). \quad (9.53)$$

This then means that, for an inhomogeneous system,

$$U_{\text{xc}}^{\text{LSD}}[n] = \int d^3r u_{\text{xc}}^{\text{unif}}(r_s(\mathbf{r}), \zeta(\mathbf{r})) = N \int_0^\infty du u \langle n_{\text{xc}}^{\text{LSD}}(u) \rangle, \quad (9.54)$$

where

$$\langle n_{\text{xc}}^{\text{LSD}}(u) \rangle = \frac{1}{N} \int d^3r n(\mathbf{r}) \frac{d\Omega_u}{4\pi} n_{\text{xc}}^{\text{unif}}(r_s(\mathbf{r}), \zeta(\mathbf{r}); u) \quad (9.55)$$

is the system- and spherically-averaged hole within LSD.

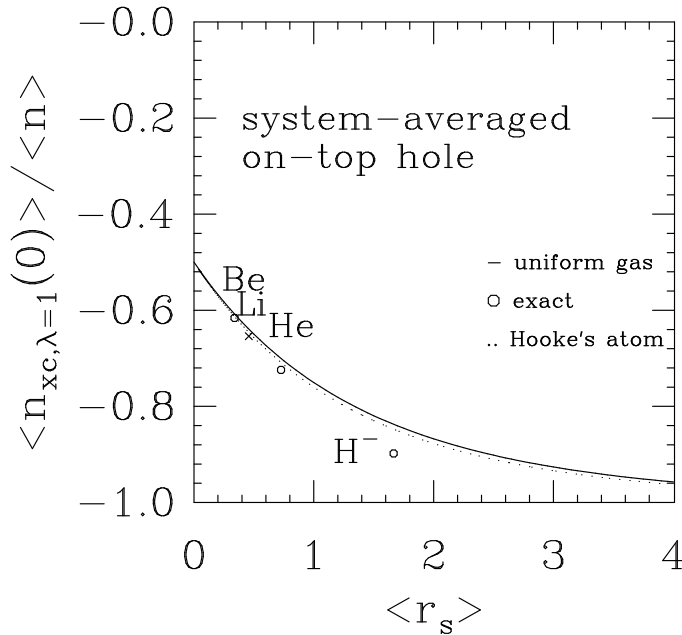


Figure 9.13: Universal curve for the system-averaged on-top hole density in spin-unpolarized systems. The solid curve is for the uniform gas. The circles indicate values calculated within LSD, while the crosses indicate essentially exact results, and the plus signs indicate less accurate CI results.

Why should this hole look similar to the true hole? Firstly, note that, because the uniform gas is an interacting many-electron system, its hole satisfies the same conditions all holes satisfy. Thus the uniform gas exchange hole integrates to -1, and its correlation hole integrates to zero. Furthermore, its exchange hole can never be negative. Also, the

ontop hole ($u = 0$) is very well approximated within LSD. For example, in exchange,

$$n_x(\mathbf{r}, \mathbf{r}) = - \left(n_{\uparrow}^2(\mathbf{r}) + n_{\downarrow}^2(\mathbf{r}) \right) / n(\mathbf{r}) \quad (9.56)$$

i.e., the ontop exchange hole is *exact* in LSD. Furthermore, for any fully spin-polarized or highly-correlated system,

$$n_{xc}(\mathbf{r}, \mathbf{r}) = -n(\mathbf{r}) \quad (9.57)$$

i.e., the ontop hole becomes as deep as possible (this makes $P(\mathbf{r}, \mathbf{r}) = 0$), again making it exact in LSD. It has been shown to be highly accurate for exchange-correlation for most systems, although not exact in general. Then, with an accurate ontop value, the cusp condition, which is also satisfied by the uniform gas, implies that the first derivative w.r.t. u at $u = 0$ is also highly accurate. In Fig. 9.13, we plot the system-averaged ontop hole for several systems where it is accurately known. For these purposes, it is useful to define the system-averaged density:

$$\langle n(u) \rangle = \frac{1}{N} \int \frac{d\Omega_u}{4\pi} \int d^3r \, n(\mathbf{r}) \, n(\mathbf{r} + \mathbf{u}). \quad (9.58)$$

and a system-averaged mean r_s value:

$$\langle r_s \rangle = \frac{\int d^3r \, n^2(\mathbf{r}) \, r_s(\mathbf{r})}{\int d^3r \, n^2(\mathbf{r})}. \quad (9.59)$$

Clearly, the system-averaged ontop hole is very accurate in LSD.

That LSD is most accurate near $u = 0$ can be easily understood physically. At u grows $\mathbf{r}'$ gets further and further away from $\mathbf{r}$. But in LSD, our only inputs are the spin-densities at $\mathbf{r}$, and so our ability to make an accurate estimate using only this information suffers. Indeed, as mentioned above, at large separations the pair-correlation function has qualitatively different behavior in different systems, so that LSD is completely incorrect for this quantity. Thus, we may expect LSD to be most accurate for small u , as indeed it is. But even at large u , its behavior is constrained by the hole normalization sum-rule.

Two other points are salient. The exchange-correlation hole in the uniform gas must be spherical, by symmetry, whereas the true hole is often highly aspherical. But this is irrelevant, since it is only the spherical-average that occurs in E_{xc} . Furthermore, the accuracy of LSD can fail in regions of extreme gradient, such as near a nucleus or in the tail of a density. But in the former, the phase-space in the system-average is small, while in the latter, the density itself is exponentially small. The same argument applies to large separations: even if g is badly approximated by LSD, it is $-n(\mathbf{r} + \mathbf{u})g(\mathbf{r}, \mathbf{r} + \mathbf{u})$ that appears in the hole, and this vanishes rapidly, both exactly and in LSD. Thus limitations of LSD in extreme situations do not contribute strongly to the exchange-correlation energy.

This then is the explanation of LSD's reliability. The energy-density of the uniform gas contains, embedded in it, both the sum-rule and the accurate ontop hole information. For most systems, this implies that their exact system-averaged hole looks very like its LSD approximation, with only small differences in details, but never with very large differences.

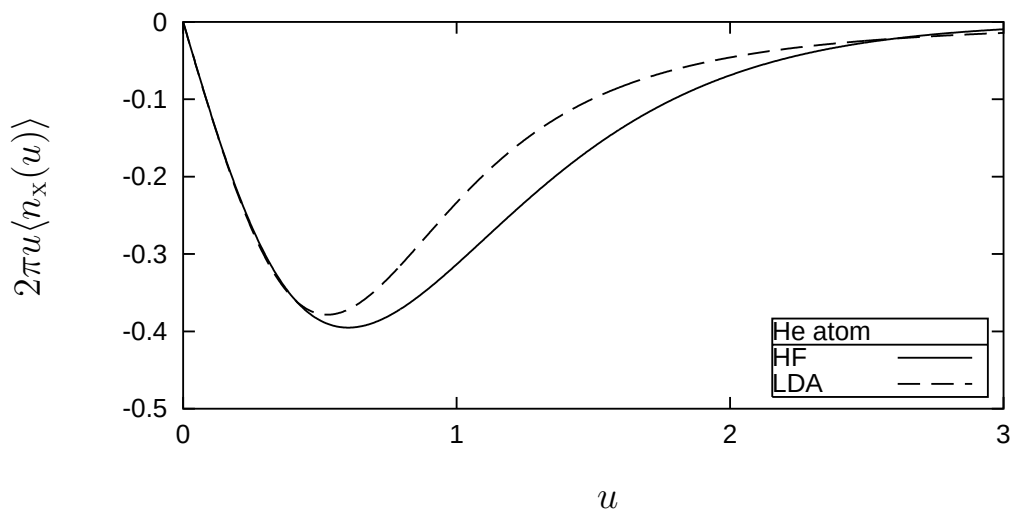


Figure 9.14: System-averaged exchange hole density (in atomic units) in the He atom, in LDA (dashed) and exactly (HF - solid). The area under each curve is the exchange energy.

In Figs. 9.14-9.15, we plot the system-averaged exchange and potential-correlation holes for the He atom, both exactly and in LSD. Each is multiplied by a factor of $2\pi u$, so that its area is just the exchange or correlation energy contribution (per electron). We see that LSD is exact for small u exchange, and typically underestimates the hole in the all-important moderate u region, while finally dying off too slowly at large u . For correlation, we see that the LSD hole is always negative in the energetically significant regions, whereas the true hole has a significant positive bump near $u = 1.5$. This is yet another explanation of the large overestimate of LSD correlation. In the next chapter, we will show how to use the failed gradient expansion to improve the description of the hole, and so construct a generalized gradient approximation.

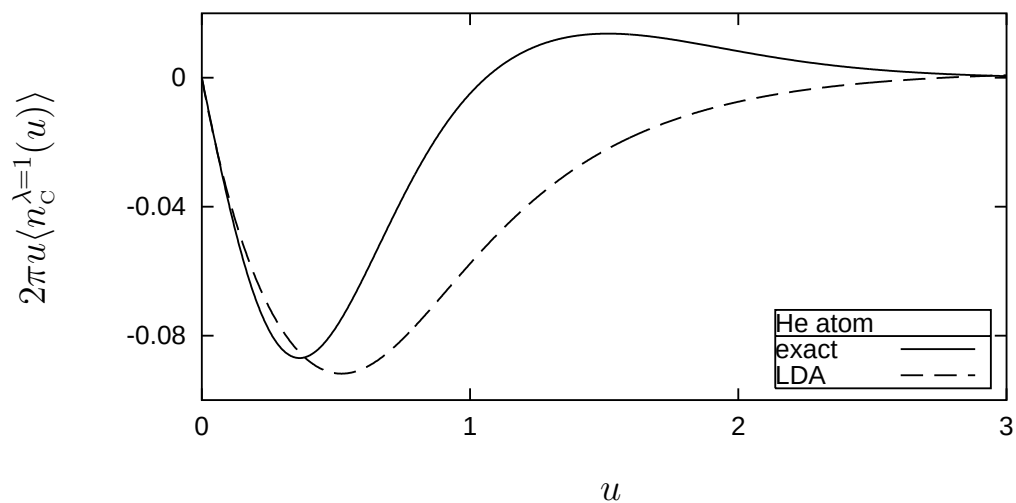


Figure 9.15: System-averaged correlation hole density at full coupling strength (in atomic units) in the He atom, in LSD, numerical GGA, and exactly (CI). The area under each curve is the full coupling-strength correlation energy.

Chapter 10

Generalized gradient approximations

¹ In this chapter, we first discuss in more detail why the gradient expansion fails for finite systems, in terms of the exchange-correlation hole. Fixing this leads directly to a generalized gradient approximation (GGA) that is numerically defined, and corrects many of the limitations of GEA for finite systems. We then discuss how to represent some of the many choices of forms for GGA, using the enhancement factor. We can understand the enhancement factor in terms of the holes, and then understand consequences of gradient corrections for chemical and physical systems. Finally we mention other popular GGAs not constructed in this fashion.

10.1 Fixing the holes: Exchange

We begin with exchange. We have seen that LSD works by producing a good approximation to the system- and spherically-averaged hole near $u = 0$, and then being a controlled extrapolation into the large u region. The control comes from the fact that we are modelling the hole by that of another physical system, the uniform gas. Thus the LSD exchange hole is normalized, and everywhere negative. When we add gradient corrections, the model for the hole is no longer that of any physical system. In particular, its behavior at large separations goes bad. In fact, the gradient correction to the exchange hole can only be normalized with the help of a convergence factor.

To see this, consider Fig. 10.1, which shows the spherically averaged exchange hole for a given reduced gradient of $s = 1$. Everything is plotted in terms of dimensionless separation, $z = 2k_F u$. The region shown is the distance to the first maximum in the LDA hole, where it just touches zero for the first time. The GEA correction correctly deepens the hole at small u , but then contains large oscillations at large u . These oscillations cause the GEA hole to unphysically become positive after $z = 6$. These oscillations are so strong that they require some damping to make them converge. Without a damping factor, the gradient correction to the exchange energy from this hole is undefined.

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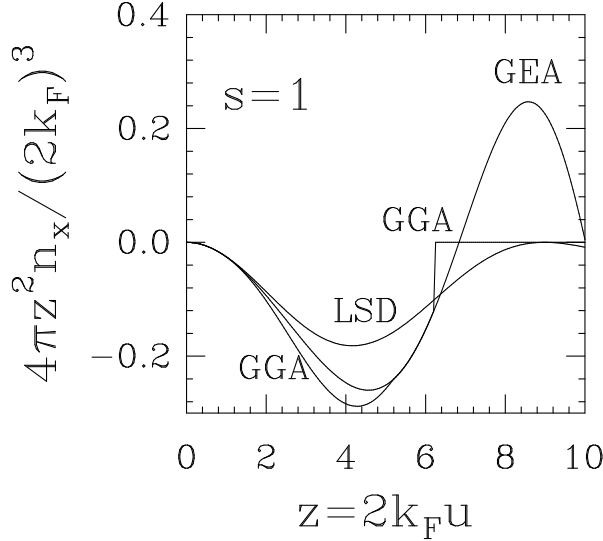


Figure 10.1: Spherically-averaged exchange hole density $n_x^{\text{sph.av.}}(u)$ for $s = 1$.

The real-space cutoff construction of the generalized gradient approximation (GGA), is to include only those contributions from the GEA exchange hole that are negative, and to truncate the resulting hole at the first value of u which satisfies the sum-rule. In the figure, for small z , the GGA hole becomes more negative than GEA, because in some directions, the GEA hole has become positive, and these regions are simply sliced out of GGA, leading to a more negative spherically-averaged hole. Then, at about $2k_F u = 6.4$, the hole is truncated, because here the normalization integral equals -1, and its energy density contribution calculated.

We note the following important points:

- Simply throwing away positive contributions to the GEA exchange hole looks very ugly in real space. But remember we are only trying to construct a model for the spherical- and system-average. Thus although that has happened in some directions for small z , the spherically-averaged result remains smooth.
- By throwing out positive GEA contributions, a significantly larger energy density is found for moderate values of s . Even for very small s , one finds corrections. Even when GEA corrections to the LSD hole are small, there are always points at which the LSD hole vanishes. Near these points, GEA can make a positive correction, and so need fixing. This means that even as $s \rightarrow 0$, the GGA energy differs from GEA.
- For very large s (e.g. greater than 3), the wild GEA hole produces huge corrections to LSD, the normalization cutoff becomes small, and limits the growth of the energy density. However, this construction clearly cannot be trusted in this limit, since even

a small distance away from $u = 0$ may have a completely different density.

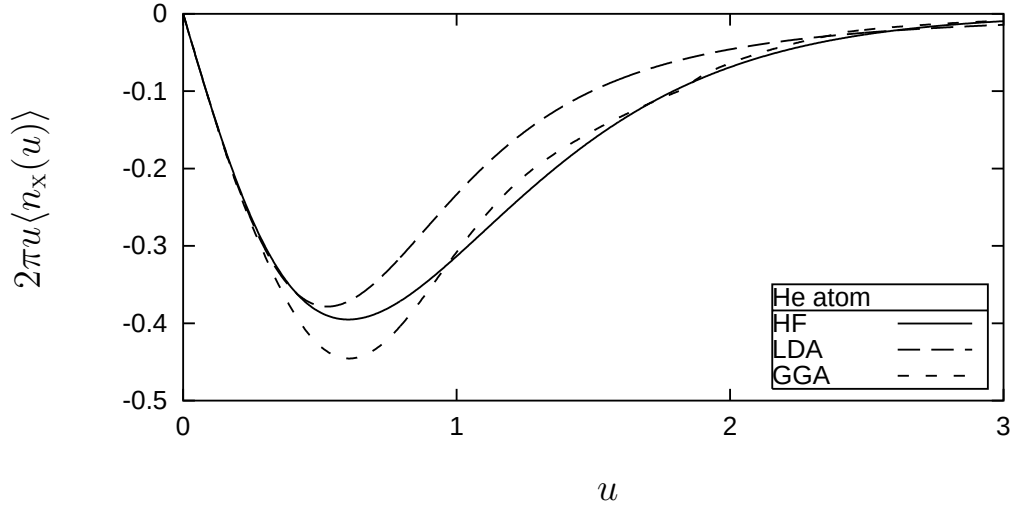


Figure 10.2: System-averaged exchange hole density (in atomic units) in the He atom. The exact curve (solid) is Hartree-Fock, the long dashes denote LDA, and the short dashes are real-space cutoff GGA. The area under each curve is the exchange energy.

The results of the procedure are shown in Fig. 10.2. We see that the LDA underestimate is largely cured by the procedure, resulting in a system-averaged hole that matches the exact one better almost everywhere.

There is a simple way to picture the results. We have seen how the spin-scaling relation means that one need only devise a total density functional, and its corresponding spin-dependence follows. Furthermore, since it scales linearly, the only way in which it can depend on the first-order gradient is through s , the reduced dimensionless gradient. Thus we may write any GGA for exchange, that satisfies the linear scaling relation, as

$$E_x^{\text{GGA}}[n] = \int d^3r \, e_x^{\text{unif}}(n(\mathbf{r})) F_x(s(\mathbf{r})) \quad (10.1)$$

The factor F_x is the exchange enhancement factor, and tells you how much exchange is enhanced over its LDA value. It is the analog of $F_{xc}^{\text{unif}}(r_s)$ from before. In Fig. 10.3, we plot various enhancement factors. First note that $F_x = 1$ corresponds to LDA. Then the dashed line is GEA, which has an indefinite parabolic rise. The solid line is the result of the real-space cutoff procedure. It clearly produces a curve whose enhancement is about double that of GEA for small and moderate s , because of the elimination of positive contributions to the hole. But the hole-GGA curve also grows less rapidly at large s , because of the normalization cutoff.

Also included in the figure are two modern GGAs, (Becke 88 and Perdew-Wang 91) that we discuss more later. They both agree with the general shape of the hole-GGA for moderate values of s , making the real-space cutoff procedure a justification for any of them. The most significant deviation in this region is that the hole-GGA has an upward

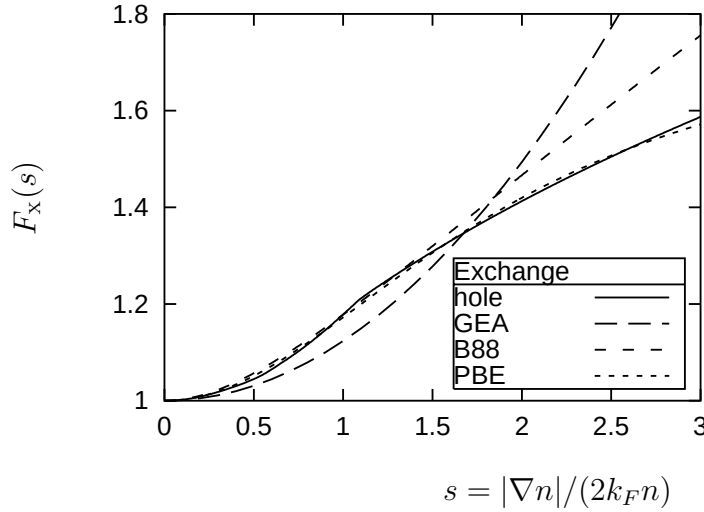


Figure 10.3: Exchange enhancement factors for different GGA's

bump near $s = 1$. This is due to the negativity and normalization cutoffs meeting, as is about to happen in Fig. ?? for slightly larger s , and is an artifact of the crude construction. Recalling that GGA is still an approximation, the differences between different GGA's are probably of the order of the intrinsic error in this approximate form.

10.2 Fixing the holes: Correlation

The case for correlation is very similar. Here there is no negativity constraint, and the real-space construction of the GGA correlation hole simply corrects the lack of normalization in the GEA correlation hole. Fig. 10.4 shows what happens. The line marked 0 is the LDA correlation hole. Note its diffuseness. Here the natural length scale is not $k_F u$, but rather $k_s u$, because we are talking about correlation. Similarly reduced gradients are measured relative to this length scale. The other curves are GEA holes for increasing reduced gradients. Note that the GEA hole is everywhere positive, leading to consistently positive corrections to LDA energies. Note also how large it becomes at say $t = 1.5$, producing a strongly positive energy contribution. For small reduced gradients, the gradient correction to the hole is slight, and has little effect on the LSD hole, until at large distances, it must be cutoff. As the gradient grows, the impact on the LSD hole becomes much greater, and the cutoff shrinks toward zero. Since the energy density contribution is weighted toward $u = 0$ relative to this picture, and all curves initially drop, the GGA correlation hole always produces a negative correlation energy density.

In Fig. 10.5, we see the results for the system-averaged hole, which are even more dramatic than the exchange case. At small separations, the GEA correctly makes the LDA hole less deep, as expected. But now, instead of producing a wild (i.e., unnormalized) positive peak, the positive contribution is much less pronounced, and is controlled by the

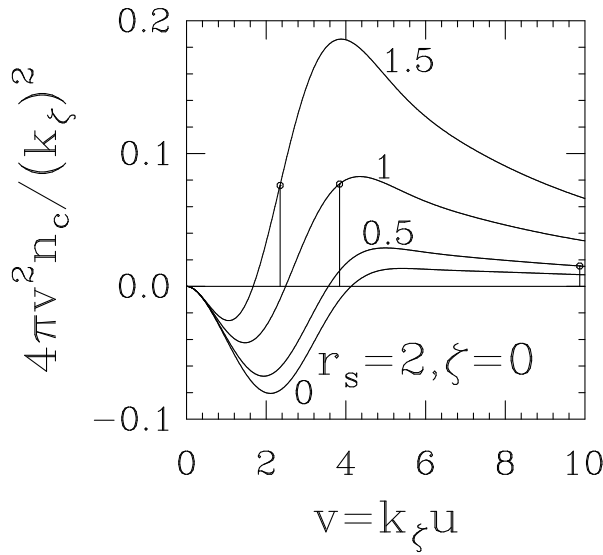


Figure 10.4: Spherically-averaged correlation hole density n_c for $r_s = 2$ and $\zeta = 0$. GEA holes are shown for four values of the reduced density gradient, $t = |\nabla n|/(2k_s n)$. The vertical lines indicate where the numerical GGA cuts off the GEA hole to make $\int_0^{v_c} dv \, 4\pi v^2 n_c(v) = 0$.

normalization. The upward bump and rapid turnoff beyond $u = 2$ are artifacts of the crude real-space cutoff procedure, and remind us of how little we know of the details of the corrections to LDA. But the overall effect on the energy is very satisfying. The LDA hole spreads out enormously, giving rise to a correlation energy that is at least a factor of 2 too deep, while the real-space cutoff hole has produced something similar to the true hole.

10.3 Visualizing and understanding gradient corrections

To understand gradient corrections for exchange-correlation, we begin with the spin-unpolarized case, where we write

$$E_{xc}^{\text{GGA}}[n] = \int d^3r \, e_x^{\text{unif}}(n(\mathbf{r})) \, F_{xc}(r_s(\mathbf{r}), s(\mathbf{r})). \quad (10.2)$$

This enhancement factor contains all our others as special cases:

$$F_{xc}(r_s, s = 0) = F_{xc}^{\text{unif}}(r_s), \quad F_{xc}(r_s = 0, s) = F_x(s). \quad (10.3)$$

We plot it for the case of the PBE functional in Fig 10.6. We will discuss the various kinds of GGA functionals that have been developed and are in use later, but for now we simply note that this GGA was designed to recover the GGA for the real-space correction

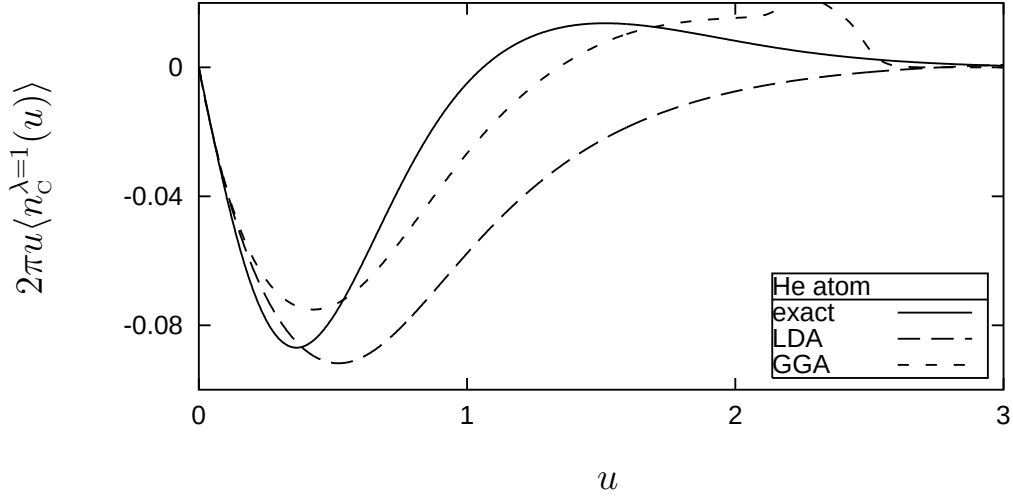


Figure 10.5: System-averaged correlation hole density at full coupling strength (in atomic units) in the He atom. The exact curve (solid) is from a CI calculation, the long dashed is LDA, and the short-dashes are real-space cutoff GGA. The area under each curve is the potential contribution to correlation energy.

of the GEA hole for moderate s , and includes also several other energetically significant constraints.

These curves contain all the physics (and ultimately) chemistry behind GGA's. We make the following observations:

- Along the y -axis, we have $F_{\text{xc}}^{\text{unif}}(r_s)$, the uniform gas enhancement factor.
- The effect of gradients is to enhance exchange. We have already seen this in action in the previous sections. Essentially, in the positive direction of the gradient, the density is increased, while dropping on the opposite side. This allows the center of the hole to move in that direction, becoming deeper due to the higher density, and yielding a higher exchange energy density.
- The effect of gradients is turn off correlation relative to exchange. This is because, in regions of high gradient the exchange effect keeps electrons apart, so that their correlation energy becomes relatively smaller. In our real-space analysis of the hole, we see that large gradients ultimately eliminate correlation.
- A simple picture of the correlation effects is given by the observation that for t up to about 0.5, the GGA make little correction to LDA, but then promptly cuts off correlation as t grows, as in Fig. ?? . But t is the reduced gradient for correlation, defined in terms of the screening wavevector, not the Fermi wavevector. For an unpolarized system:

$$t = \frac{|\nabla n|}{2k_s n} = \frac{k_F}{k_s} s \approx \sqrt{\frac{1.5}{r_s}} s \quad (10.4)$$

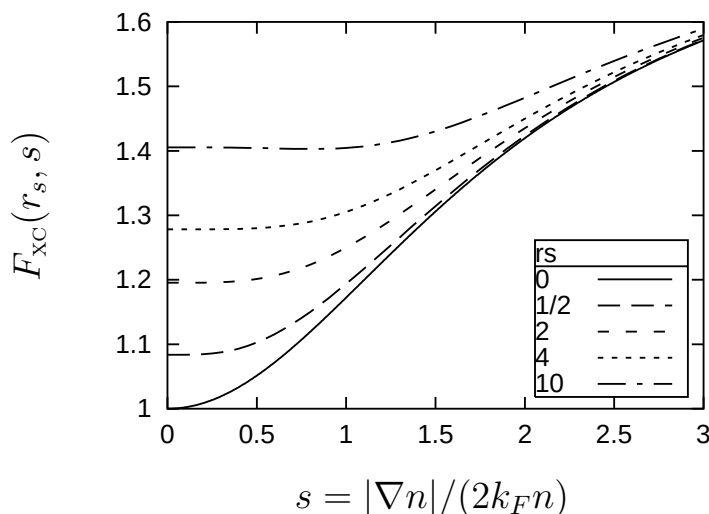


Figure 10.6: Exchange-correlation enhancement factors for the PBE GGA.

Thus, for r_s about 2, $t = s$, and we see correlation turning off at t about 0.5. For $r_s = 10$, $t \approx 0.4s$, so that correlation turns off about $s = 1.2$, while for $r_s = 1/2$, $t \approx 1.7s$, so that correlation turns off very quickly, at s about 0.3.

- An interesting consequence of the point above is that pure exchange is the *least* local curve, and that as correlation is turned on, the functional becomes more local, i.e., closer to the LDA value, both in the sense that gradient corrections become significant at larger s values, and also that even when they do, their magnitude is less.

We can repeat this analysis to understand the effects of spin polarization. Must fill this in.

Exercise 58 Deduce the maximum value for F_{XC} allowed by the Lieb-Oxford bound.

Exercise 59 The lines of different r_s values never cross in Fig. Y. What does this imply about the functional?

10.4 Effects of gradient corrections

In this section, we survey some of the many properties that have been calculated in DFT electronic structure calculations, and try to understand the errors made LSD, and why GGA corrects them the way it does.

- Both the large underestimate in the magnitude of total exchange energies and the overestimate in the magnitude of correlation energies can be seen immediately from Fig. 10.6. Ignoring gradients ignores the enhancement of exchange and the truncation of correlation.

- In studying ionization energies of atoms, one finds LSD overbinds s electrons relative to p , p relative to d , and so forth. Since core electrons have higher density than outer ones, the local approximation is less accurate for them.
- When a molecule is formed from atoms, the density becomes more homogeneous than before. The region of the chemical bond is flatter than the corresponding regions of exponential decay in atoms. Thus LDA makes less of an underestimate of the energy of a molecule than it does of the constituent atoms. Write

$$E_{\text{xc}}(\text{system}) = E_{\text{xc}}^{\text{LDA}}(\text{system}) + \Delta E_{\text{xc}}^{\text{LDA}}(\text{system}) \quad (10.5)$$

Then $\Delta E_{\text{xc}}(\text{atoms}) < \Delta E_{\text{xc}}(\text{molecules})$, remembering that both are negative. The atomization energy of a molecule is

$$E_{\text{xc}}^{\text{atmiz}} = E_{\text{xc}}(\text{molecule}) - E_{\text{xc}}(\text{atoms}) \quad (10.6)$$

so that

$$E_{\text{xc}}(\text{atom}) = E_{\text{xc}}^{\text{LDA}}(\text{atom}) + \Delta E_{\text{xc}}^{\text{LDA}}(\text{molecule}) - E_{\text{xc}}^{\text{LDA}}(\text{atom}) \quad (10.7)$$

Thus molecules are overbound in LDA, typically by as much as 30 kcal/mol.

- Transition state barriers can be understood in much the same way. A typical transition state in quantum chemistry is one of higher symmetry and coordination than the reactants. Thus comparing the transition state to the reactants, in just the way done above for a bond and its constituent atoms, we find that the transition-state barrier, defined as

$$E_{\text{xc}}^{\text{trans}} = -E_{\text{xc}}(\text{reactants}) + E_{\text{xc}}(\text{transitionstate}) \quad (10.8)$$

will be too low in an LDA calculation, and be raised by a GGA calculation. Notice though that this depends on the coordination argument. If the transition state is less coordinated, the result is the reverse: LDA overestimates the barrier, and GGA will weaken it. This is often the case for, eg. surface diffusion, where the transition state (e.g. bridge-bonded) has lower symmetry than the initial state (e.g. atop bonded).

- By the same reasoning as for atomization energies, consider the process of stretching a bond. As a bond is stretched, LDA's overbinding tendency will reduce. Thus equilibrium bond lengths are usually too small in LDA, and GGA stretches them. The only exception to this is the case of bonds including H atoms. One can show that typically GGA favors a process in which

$$\frac{\Delta \langle s \rangle}{\langle s \rangle} \geq P \frac{\Delta \langle r_s \rangle}{2 \langle r_s \rangle} + Q \Delta |\zeta|, \quad (10.9)$$

where $\langle s \rangle$, etc., are precisely chosen averages, and where P is typically close to 1, and $Q \approx 0$. Usually fractional changes in the density are very small, due to the presence

of core electrons, and the right hand side is thought of as zero. This leads to the generic claim that GGA prefers inhomogeneity, i.e., LDA overfavors homogeneity. For example, in our cases above, when a molecule is atomized, its mean gradient increases. The inequality means that GGA will like this more than LDA, and so have a smaller atomization energy.

Neglecting the right-hand-side works for all atomization energies, in which the changes are large. But for a bond-stretch, the fractional gradient changes are much smaller. In the case of H atoms, the density is sufficiently low as to make its fractional change larger than that of the gradient, when stretching a bond with an H atom. Thus in that case, the gradient corrections have the reverse effect, and those bonds are shortened.

10.5 Satisfaction of exact conditions

We can now look back on the previous chapters, and check that the real-space cutoff GGA satisfies conditions that LDA satisfies, and maybe a few more.

- **Size-consistency** Obviously, GGA remains size consistent.

- **The Lieb-Oxford bound.**

The LO bound gives us a maximum value for the enhancement factor of 1.804. The real-space cutoff will eventually violate this bound, but only at large s , where we do not trust it anyhow.

- **Coordinate scaling**

For exchange, clear $\cos$ only s dependence.

Show F_{xc} lines never cross.

- **Virial theorem** Trivially true.

- **High-density correlation**

The numerical GGA satisfies this condition. As we show below, many chemical systems are close to this, and, by truncating the long-ranged Coulomb correlation hole, numerical GGA yields a finite value.

- **Self-interaction error**

Simple density functionals like LDA and GEA naturally have a self-interaction error, because they cannot tell when there is only one electron in the system. While GGA might improve numerically the value of E_x or E_c for that one electron, it will still have a residual self-interaction error.

- **Symmetry dilemma**

Just as above, nothing in GGAs construction helps here.

- **Potentials**

From the naive sense...

- **Koopman's theorem** No real improvement here.

10.6 A brief history of GGA's

We have seen how the real-space cutoff construction imposed on the gradient expansion produces a numerically-defined GGA. This is not unique, in that, e.g. a smoother cutoff will lead to slightly different curves for moderate gradients, and perhaps much different curves for large gradients.

10.7 Questions about generalized gradient approximations

Chapter 11

Adiabatic connection formula, static correlation, and hybrids

¹ In this chapter, we discuss the limitations of GGA's for molecular atomization energies, and why it is useful to mix some exact exchange with a GGA calculation. This requires the introduction of another useful formal device, namely the adiabatic connection formula. But we shall see that, although it looks different here, we have already come across this, in the scaling relations we found in chapter ??.

11.1 Coupling constant for one electron

Introduce a parameter in $\hat{H}$, say λ . Then all eigenstates and eigenvalues depend on λ , i.e., Eq. (1.9) becomes:

$$\hat{H}^\lambda \phi^\lambda = \varepsilon^\lambda \phi^\lambda. \quad (11.1)$$

Most commonly,

$$\hat{H}^\lambda = \hat{T} + \lambda \hat{V}, \quad 0 < \lambda < \infty. \quad (11.2)$$

A λ in front of the potential is often called the coupling constant, and then all eigenvalues and eigenfunctions depend on λ . For example, for the harmonic oscillator of force constant $k = \omega^2$, the ground-state wavefunction is $\phi(x) = (\omega/\pi)^{1/4} \exp(-\omega x^2/2)$. Since $V(x) = kx^2/2$, $\lambda V(x) = \lambda kx^2/2$, i.e., the factor of λ multiplies k . Then $\omega \rightarrow \sqrt{\lambda}\omega$, and so

$$\phi^\lambda(x) = \left(\frac{\sqrt{\lambda}\omega}{\pi} \right)^{1/4} \exp(-\sqrt{\lambda}\omega x^2/2) \quad (\text{harmonic oscillator}). \quad (11.3)$$

For a λ -dependent Hamiltonian, we can differentiate the energy with respect to λ . Because the eigenstates are variational extrema, the contributions due to differentiating the wavefunctions with respect to λ vanish, leaving

$$\frac{dE^\lambda}{d\lambda} = \langle \phi^\lambda | \frac{\partial \hat{H}^\lambda}{\partial \lambda} | \phi^\lambda \rangle. \quad (11.4)$$

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Thus

$$E = E^{\lambda=1} = E^{\lambda=0} + \int_0^1 d\lambda \langle \phi^\lambda | \frac{\partial \hat{H}^\lambda}{\partial \lambda} | \phi^\lambda \rangle. \quad (11.5)$$

Furthermore, if λ simply multiplies $\hat{V}$, then

$$\frac{dE^\lambda}{d\lambda} = \langle \phi^\lambda | \hat{V} | \phi^\lambda \rangle, \quad (11.6)$$

so that

$$E = E^{\lambda=0} + \int_0^1 d\lambda \langle \phi^\lambda | \hat{V} | \phi^\lambda \rangle. \quad (11.7)$$

This is often called the Hellmann-Feynman theorem.

Exercise 60 Hellmann-Feynman theorem

Show that the 1-d H-atom and 1-d harmonic oscillator satisfy the Hellman-Feynman theorem. How does the approximate solution using a basis set do?

11.2 Adiabatic connection formula

Now we apply the same thinking to DFT. When doing so, we always try to keep the density fixed (or altered only in some simple way), and not include the external potential. The adiabatic connection formula is a method for continuously connecting the Kohn-Sham system with the physical system. Very simply, we introduce a coupling constant λ into the universal functional, to multiply V_{ee} :

$$F^\lambda[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \lambda \hat{V}_{ee} | \Psi \rangle \quad (11.8)$$

For $\lambda = 1$, we have the physical system. For $\lambda = 0$, we have the Kohn-Sham system. We can even consider $\lambda \rightarrow \infty$, which is a highly correlated system, in which the kinetic energy is negligible. But for all values of λ , the density remains that of the physical system. Note that this implies that the external potential is a function of λ : $v_{\text{ext}}^\lambda(\mathbf{r})$. We denote $\Psi^\lambda[n]$ as the minimizing wavefunction for a given λ . We can generalize all our previous definitions, but we must do so carefully. By a superscript λ , we mean the expectation value of an operator on the system with coupling-constant λ . Thus

$$T^\lambda[n] = \langle \Psi^\lambda[n] | \hat{T} | \Psi^\lambda[n] \rangle, \quad (11.9)$$

but

$$V_{ee}^\lambda[n] = \langle \Psi^\lambda[n] | \lambda \hat{V}_{ee} | \Psi^\lambda[n] \rangle. \quad (11.10)$$

The Kohn-Sham quantities are independent of λ , so

$$E_{\text{xc}}^\lambda[n] = \langle \Psi^\lambda[n] | \hat{T} + \lambda \hat{V}_{ee} | \Psi^\lambda[n] \rangle - \langle \Phi[n] | \hat{T} + \lambda \hat{V}_{ee} | \Phi[n] \rangle \quad (11.11)$$

Exercise 61 Coupling constant dependence of exchange

Show that

$$U^\lambda[n] = \lambda U[n], \quad E_x^\lambda[n] = \lambda E_x[n], \quad (11.12)$$

i.e., both Hartree and exchange energies have a linear dependence on the coupling-constant.

Our next step is to write the Hellmann-Feynman theorem for this λ -dependence in the Hamiltonian. We write

$$F[n] = T_s[n] + \int_0^1 d\lambda \langle \Psi^\lambda[n] | \hat{V}_{ee} | \Psi^\lambda[n] \rangle \quad (11.13)$$

where $F[n] = F^{\lambda=1}[n]$, $T_s[n] = F^{\lambda=0}[n]$. The derivative w.r.t. λ of $F^\lambda[n]$ is just the derivative of the operator w.r.t. λ , because $\Psi^\lambda[n]$ is a minimizing wavefunction at each λ , just as in the one-electron case. Inserting the definition of the correlation energy, we find

$$\begin{aligned} E_{xc}[n] &= \int_0^1 d\lambda \langle \Psi^\lambda[n] | \hat{V}_{ee} | \Psi^\lambda[n] \rangle - U[n] \\ &= \int_0^1 \frac{d\lambda}{\lambda} U_{xc}^\lambda[n] = \int_0^1 d\lambda U_{xc}[n](\lambda), \end{aligned} \quad (11.14)$$

where we have used $V_{ee}^\lambda = \lambda \langle \Psi^\lambda[n] | \hat{V}_{ee} | \Psi^\lambda[n] \rangle$ and $U^\lambda = \lambda U$, and introduced the simple notation $U_{xc}(\lambda) = U_{xc}^\lambda/\lambda$ for later convenience. Thus we have written the exchange-correlation energy as a solely potential contribution, but at the price of having to evaluate it at all intermediate coupling constants. We will see shortly that this price actually provides us with one of our most important tools for analyzing density functionals.

The integrand in the adiabatic connection formula for a given physical system is sketched in Fig. 11.1. The curve itself is given by the solid line, and horizontal lines have been drawn at the value at $\lambda = 0$ and at $\lambda = 1$. We can understand this figure by

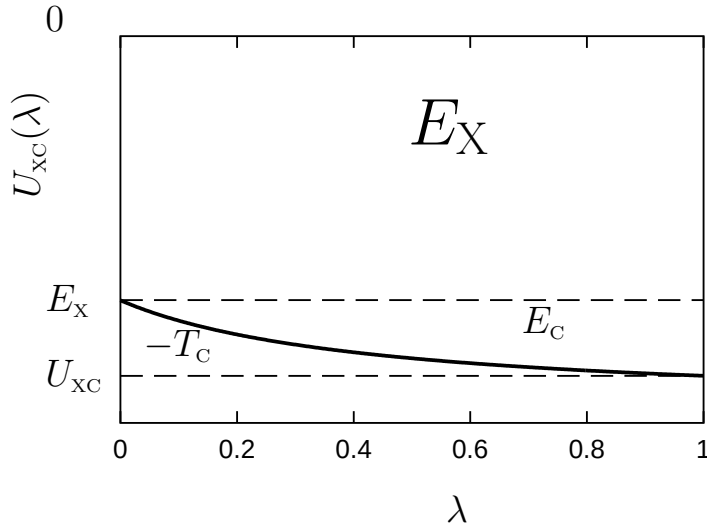


Figure 11.1: Cartoon of the adiabatic connection integrand

making several key observations:

- The value at $\lambda = 0$ is just E_x .
- The value at $\lambda = 1$ is just $E_x + U_c$.
- The area between the curve and the x -axis is just E_{xc} .
- The area beneath the curve, between the curve and a horizontal line drawn through the value at $\lambda = 1$, is just T_c .

Thus the adiabatic connection curve gives us a geometrical interpretation of many of the energies in density functional theory.

To demonstrate the usefulness of adiabatic decomposition, we show this curve for the He atom in Fig. 11.2. Note first the solid, exact line. It is almost straight on this scale.

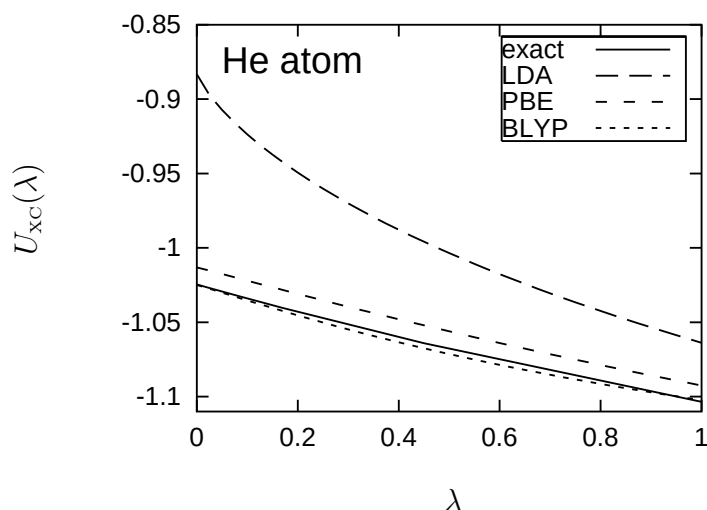


Figure 11.2: Adiabatic decomposition of exchange-correlation energy in He for several functional approximations.

This is telling us that this system is weakly correlated, as we discuss below. We can also understand LDA in more detail. Clearly, this functional improves with λ . This causes the cancellation of errors between exchange and correlation, since the area under the curve will then be more accurate than the value at $\lambda = 0$. Why this happens will be discussed later. But for now, we simply note that the statement that LDA improves with λ is equivalent to the cancellation of errors statement, but is much more transparent.

In principle, we can cast all discussion of these curves in terms of coupling-constants, and analyze all approximate functionals this way. In practice, there is a far more intuitively appealing approach, analyzing functionals in terms of their dependence on their arguments, as we see in the following sections.

11.3 Relating scaling to coupling constant for one electron

In modern density functional theory, one of the most important relationships is between the coupling constant and coordinate scaling. We can see this for these simple 1-d problems. The Schrödinger equation at coupling constant λ is

$$(\hat{T} + \lambda \hat{V}(x)) \phi^\lambda(x) = E^\lambda \phi^\lambda(x) \quad (11.15)$$

If we replace x by γx everywhere, we find

$$\left(\frac{1}{\gamma^2} \hat{T} + \lambda \hat{V}(\gamma x) \right) \phi^\lambda(\gamma x) = E^\lambda \phi^\lambda(\gamma x) \quad (11.16)$$

Furthermore, if $\hat{V}$ is homogeneous of degree p ,

$$(\hat{T} + \lambda \gamma^2 \gamma^p \hat{V}(x)) \phi^\lambda(\gamma x) = \gamma^2 E^\lambda \phi^\lambda(\gamma x) \quad (11.17)$$

Thus, if we choose $\lambda \gamma^{p+2} = 1$, then Eq. (11.17) is just the normal Schrödinger equation, and we can identify $\phi^\lambda(\gamma x)$, which is equal (up to normalization) to $\phi_\gamma^\lambda(x)$ with $\phi(x)$. If we scale both of these by $1/\gamma$, we find

$$\phi^\lambda(x) = \phi_{1/\gamma}(x) = \phi_{\lambda^{1/(p+2)}}(x) \quad (11.18)$$

In this case, changing coupling constant by λ is equivalent to scaling by $\lambda^{1/4}$, but this relation depends on the details of the potential.

Exercise 62 λ -dependence

Show that, for a homogeneous potential of degree p ,

$$E^\lambda = \lambda^{\frac{2}{p+2}} E \quad (11.19)$$

Exercise 63 λ -dependence of 1-d H

Find the coupling-constant dependence for the wavefunction and energy for the 1-d H-atom, $V(x) = -\delta(x)$, and for the 1-d harmonic oscillator, $V(x) = \frac{1}{2}x^2$.

11.4 Relation between coupling-constant and scaling in DFT

A third important concept is the relation between scaling and coupling constant. Consider $\Psi^\lambda[n]$, which minimizes $\hat{T} + \lambda \hat{V}_{ee}$ and has density $n(\mathbf{r})$. Then $\Psi_\gamma^\lambda[n]$ minimizes $\hat{T}/\gamma^2 + (\lambda/\gamma) \hat{V}_{ee}$ and has density $n_\gamma(\mathbf{r})$. If we choose $\gamma = 1/\lambda$, we find $\Psi_{1/\lambda}^\lambda[n]$ minimizes $\lambda^2(\hat{T} + \hat{V}_{ee})$ and has density $n_{1/\lambda}(\mathbf{r})$. But if $\lambda^2(\hat{T} + \hat{V}_{ee})$ is minimized, then $\hat{T} + \hat{V}_{ee}$ is minimized, so that we can identify this wavefunction being simply $\Psi[n_{1/\lambda}]$. If we scale both wavefunctions by λ , we find the extremely simple but important result

$$\Psi^\lambda[n] = \Psi_\lambda[n_{1/\lambda}], \quad (11.20)$$

which tells us how to construct a wavefunction of coupling constant λ by first scaling the density by $1/\lambda$, finding the ground-state wavefunction for the scaled density, and then scaling that wavefunction back to the original size.

This argument also leaves a simple relation for the energies:

$$F^\lambda[n] = \lambda^2 F[n_{1/\lambda}], \quad (11.21)$$

which shows how the λ -dependence of the universal functional (or, as we shall see, any energy component) is completely determined by its dependence on scaling the density, and which relates the scaled and unscaled physical wavefunctions, but at the price of altering the coupling constant. Contrast Eq. (11.21) with Eq. (7.15).

These relations prove to be extremely useful in analyzing functionals and their behavior. First note that we can take *any* functional and find out its scaling behavior quite easily. Then, through Eq. (11.21), applied to that functional, we can now deduce its coupling-constant dependence. For example, the adiabatic connection integrand of Eq. (??) $U_{xc}(\lambda)[n] = \lambda U_{xc}[n_{1/\lambda}]$. Finally, the adiabatic connection formula Eq. (??), and many variants, provide relations among the different components of correlation energy.

The simplest example in this regard is the non-interacting kinetic energy, which we know scales quadratically with scaling parameter. Then

$$T_s^\lambda[n] = \lambda^2 T_s[n_{1/\lambda}] = T_s[n] \quad (11.22)$$

i.e., the kinetic energy is independent of coupling constant, as it should be. Similarly,

$$E_x^\lambda[n] = \lambda^2 E_x[n_{1/\lambda}] = \lambda E_x[n] \quad (11.23)$$

which again makes sense, since E_x is constructed from the λ -independent Kohn-Sham orbitals, integrated with $\lambda/|\mathbf{r} - \mathbf{r}'|$.

Much less trivial is the relation between different components of the correlation energy. Consider Eq. (??) in differential form:

$$\frac{dE_{xc}^\lambda[n]}{d\lambda} = \langle \Psi^\lambda[n] | \hat{V}_{ee} | \Psi^\lambda[n] \rangle - U[n] \quad (11.24)$$

Then, from Eq. (11.21),

$$V_{ee}^\lambda[n] = \lambda \langle \Psi^\lambda[n] | \hat{V}_{ee} | \Psi^\lambda[n] \rangle = \lambda(U[n] + E_x[n]) + U_c^\lambda[n], \quad (11.25)$$

where we have used the linear dependence of exchange on λ , and we have written

$$E_c[n] = (T[n] - T_s[n]) + (V_{ee}[n] - U[n]) = T_c[n] + U_c[n] \quad (11.26)$$

and $T_c[n]$ is the kinetic contribution to the correlation energy, while $U_c[n]$ is the potential contribution. Inserting Eq. (11.25) into Eq. (11.24) and cancelling the trivial exchange contributions to both sides, we find

$$\frac{dE_c^\lambda[n]}{d\lambda} = U_c^\lambda[n]/\lambda \quad (11.27)$$

Finally, we rewrite this as a scaling relation. Since $E_C^\lambda[n] = \lambda^2 E_C[n_{1/\lambda}]$ and $U_C^\lambda[n] = \lambda^2 U_C[n_{1/\lambda}]$ and writing $\gamma = 1/\lambda$, we find, after a little manipulation

$$\gamma \frac{dE_C[n_\gamma]}{d\gamma} = E_C[n_\gamma] + T_C[n_\gamma]. \quad (11.28)$$

The adiabatic connection formula may be thought of as an integration of this formula between $\gamma = 1$ and $\gamma = \infty$.

Exercise 64 Generalizing scaling

Show that the more compact statement

$$\left. \frac{dE_C[n_\gamma]}{d\gamma} \right|_{\gamma=1} = E_C[n] + T_C[n] \quad (11.29)$$

implies the more general statement of Eq. (11.28).

Exercise 65 E_C from T_C

Derive a relation to extract $E_C[n]$ from $T_C[n_\gamma]$ alone. Rewrite this to get $E_C^\lambda[n]$ from $T_C^\lambda[n]$.

Exercise 66 *Use Eq. (9.11) and the scaling relations of the previous chapter to write E_C in terms of density matrices of different λ .*

We can easily scale any approximate functional, and so extract the separate contributions to the correlation energies, and test them against their exact counterparts, check limiting values, etc. A simple example is LDA. Then when $n \rightarrow n_\gamma$, $r_s \rightarrow r_s/\gamma$. Thus

$$E_C^{\text{LDA}}[n_\gamma] = \int d^3r n_\gamma(\mathbf{r}) \epsilon_C^{\text{unif}}(r_{s,\gamma}(\mathbf{r})) = \int d^3r n(\mathbf{r}) \epsilon_C^{\text{unif}}(r_s(\mathbf{r})/\gamma) \quad (11.30)$$

In the high-density limit, $\gamma \rightarrow \infty$, $\epsilon_C^{\text{unif}}(r_s/\gamma) \rightarrow \epsilon_C^{\text{unif}}(0)$. This is singular in true LDA, and is an error made by LDA. However, in the low density limit, $\epsilon_C^{\text{unif}}(r_s) = -d_0/r_s + d_1/r_s^{3/2} + \dots$, so that $E_C^{\text{LDA}}[n_\gamma] = -\gamma d_0 \int d^3r n(\mathbf{r})/r_s(\mathbf{r})$, vanishing linearly with γ , correctly. Note that in this low-density regime, correlation is so strong it scales the same as exchange.

Exercise 67 Wigner approximation:

Find the high-density limit of the Wigner approximation, and make a statement about roughly how large the correlation energy is within LDA.

Exercise 68 Changing λ :

Derive $E_{\text{xc}}^{\text{LDA},\lambda}[n]$ and $T_C^{\text{LDA}}[n]$.

11.5 Static, strong, and strict correlation

11.6 Hybrids: Mixing exact exchange with GGA

11.7 Questions about adiabatic connection formula and hybrids

1. Does the Hellmann-Feynman theorem apply to the problem of the particle in a potential $V(x) = \exp(-|x|)$?

2. What happens to a system as $\lambda \rightarrow \infty$?
3. What is the formula for $v_{\text{ext}}^\lambda[n](\mathbf{r})$ in terms of a scaled density?

Chapter 12

Other topics

12.1 Orbital functionals

12.2 Time-dependent density functional theory