Chapter Sixteen

Time Independent Perturbation Theory

$$H = H_0 + \lambda H_1$$

$$\lambda << 1$$

$$(H_0 + \lambda H_1)|\Psi_n\rangle = E_n|\Psi_n\rangle$$

$$H_0|\Phi_n\rangle = E_n^{(0)}|\Phi_n\rangle$$

$$H_{mn} = \langle\Phi_m|H|\Phi_n\rangle$$

$$H_{mn} = \langle\Phi_m|H_0 + \lambda H_1|\Phi_n\rangle$$

$$H_{mn} = E_m^{(0)}\delta_{mn} + \langle\Phi_m|\lambda H_1|\Phi_n\rangle$$

$$|\Psi_n\rangle = N(\lambda)\left\{|\Phi_n\rangle + \sum_{k\neq n} C_{nk}(\lambda)|\Phi_k\rangle\right\}$$

$$N(0) = 1, \quad C_{nk}(0) = 0$$

$$C_{nk}(\lambda) = \lambda C_{nk}^{(1)} + \lambda^2 C_{nk}^{(2)} + \ldots$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots$$

$$\left(H_0 + \lambda H_1\right)\left|\Psi_n\right\rangle = E_n\left|\Psi_n\right\rangle$$

$$\left|\Psi_n\right\rangle = N(\lambda)\left\{\left|\Phi_n\right\rangle + \sum_{k\neq n} C_{nk}(\lambda)\left|\Phi_k\right\rangle\right\}$$

$$C_{nk}(\lambda) = \lambda C_{nk}^{(1)} + \lambda^2 C_{nk}^{(2)} + \ldots$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots$$

$$\left(H_0 + \lambda H_1\right)N(\lambda)\left\{\left|\Phi_n\right\rangle + \lambda\sum_{k\neq n} C_{nk}^{(1)}(\lambda)\left|\Phi_k\right\rangle + \lambda^2\sum_{k\neq n} C_{nk}^{(2)}(\lambda)\left|\Phi_k\right\rangle + \ldots\right\}$$

$$= \left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots\right)N(\lambda)\left\{\left|\Phi_n\right\rangle + \lambda\sum_{k\neq n} C_{nk}^{(1)}(\lambda)\left|\Phi_k\right\rangle + \lambda^2\sum_{k\neq n} C_{nk}^{(2)}(\lambda)\left|\Phi_k\right\rangle + \ldots\right\}$$

$$\left(H_0+\lambda H_1\right)\left\{\left|\Phi_n\right\rangle+\lambda\sum_{k\neq n}C_{nk}^{(1)}(\lambda)\left|\Phi_k\right\rangle+\lambda^2\sum_{k\neq n}C_{nk}^{(2)}(\lambda)\left|\Phi_k\right\rangle+\ldots\right\}$$

$$=\left(E_n^{(0)}+\lambda E_n^{(1)}+\lambda^2E_n^{(2)}+\ldots\right)\left\{\left|\Phi_n\right\rangle+\lambda\sum_{k\neq n}C_{nk}^{(1)}(\lambda)\left|\Phi_k\right\rangle+\lambda^2\sum_{k\neq n}C_{nk}^{(2)}(\lambda)\left|\Phi_k\right\rangle+\ldots\right\}$$

$$H_0\sum_{k\neq n}C_{nk}^{(1)}(\lambda)\left|\Phi_k\right\rangle+H_1\left|\Phi_n\right\rangle=E_n^{(0)}\sum_{k\neq n}C_{nk}^{(1)}(\lambda)\left|\Phi_k\right\rangle+E_n^{(1)}\left|\Phi_n\right\rangle$$

$$E_n^{(1)}\left|\Phi_n\right\rangle=H_1\left|\Phi_n\right\rangle+\sum_{k\neq n}C_{nk}^{(1)}(\lambda)H_0\left|\Phi_k\right\rangle-E_n^{(0)}\sum_{k\neq n}C_{nk}^{(1)}(\lambda)\left|\Phi_k\right\rangle$$

$$E_n^{(1)}\left|\Phi_n\right\rangle=H_1\left|\Phi_n\right\rangle+\sum_{k\neq n}C_{nk}^{(1)}(\lambda)E_k^{(0)}\left|\Phi_k\right\rangle-\sum_{k\neq n}C_{nk}^{(1)}(\lambda)E_n^{(0)}\left|\Phi_k\right\rangle$$

$$E_n^{(1)}\left|\Phi_n\right\rangle=H_1\left|\Phi_n\right\rangle+\sum_{k\neq n}\left(E_k^{(0)}-E_n^{(0)}\right)C_{nk}^{(1)}(\lambda)\left|\Phi_k\right\rangle$$

$$\langle \Phi_n | \times$$

$$E_n^{(1)} | \Phi_n \rangle = H_1 | \Phi_n \rangle + \sum_{k \neq n} \left(E_k^{(0)} - E_n^{(0)} \right) C_{nk}^{(1)}(\lambda) | \Phi_k \rangle$$

$$E_n^{(1)} \langle \Phi_n | \Phi_n \rangle = \langle \Phi_n | H_1 | \Phi_n \rangle + \sum_{k \neq n} \left(E_k^{(0)} - E_n^{(0)} \right) C_{nk}^{(1)}(\lambda) \langle \Phi_n | \Phi_k \rangle$$

$$E_n^{(1)} = \langle \Phi_n | H_1 | \Phi_n \rangle + \sum_{k \neq n} \left(E_k^{(0)} - E_n^{(0)} \right) C_{nk}^{(1)}(\lambda) \delta_{nk}$$

$$E_n^{(1)} = \langle \Phi_n | H_1 | \Phi_n \rangle$$

$$E_n^{(1)} = \int d^3 r \Phi_n^*(\mathbf{r}) H_1(\mathbf{r}) \Phi_n(\mathbf{r})$$

$\langle \Phi_m | \times$

$$E_n^{(1)} |\Phi_n\rangle = H_1 |\Phi_n\rangle + \sum_{k \neq n} \left(E_k^{(0)} - E_n^{(0)} \right) C_{nk}^{(1)}(\lambda) |\Phi_k\rangle$$

$$E_n^{(1)} \langle \Phi_m | \Phi_n \rangle = \langle \Phi_m | H_1 | \Phi_n \rangle + \sum_{k \neq n} \left(E_k^{(0)} - E_n^{(0)} \right) C_{nk}^{(1)}(\lambda) \langle \Phi_m | \Phi_k \rangle$$

$$0 = \langle \Phi_m | H_1 | \Phi_n \rangle + \sum_{k \neq n} \left(E_k^{(0)} - E_n^{(0)} \right) C_{nk}^{(1)}(\lambda) \delta_{mk}$$

$$0 = \langle \Phi_m | H_1 | \Phi_n \rangle + \left(E_m^{(0)} - E_n^{(0)} \right) C_{nm}^{(1)}$$

$$C_{nm}^{(1)} = \frac{\langle \Phi_m | H_1 | \Phi_n \rangle}{E_n^{(0)} - E_m^{(0)}}$$

$$C_{nk}^{(1)} = \frac{\langle \Phi_k | H_1 | \Phi_n \rangle}{E_n^{(0)} - E_k^{(0)}}$$

$$\left(H_0+\lambda H_1\right)\left\{\left|\Phi_n\right\rangle+\lambda\sum_{k\neq n}C_{nk}^{(1)}(\lambda)\left|\Phi_k\right\rangle+\lambda^2\sum_{k\neq n}C_{nk}^{(2)}(\lambda)\left|\Phi_k\right\rangle+\ldots\right\}$$

$$=\left(E_n^{(0)}+\lambda E_n^{(1)}+\lambda^2E_n^{(2)}+\ldots\right)\left\{\left|\Phi_n\right\rangle+\lambda\sum_{k\neq n}C_{nk}^{(1)}(\lambda)\left|\Phi_k\right\rangle+\lambda^2\sum_{k\neq n}C_{nk}^{(2)}(\lambda)\left|\Phi_k\right\rangle+\ldots\right\}$$

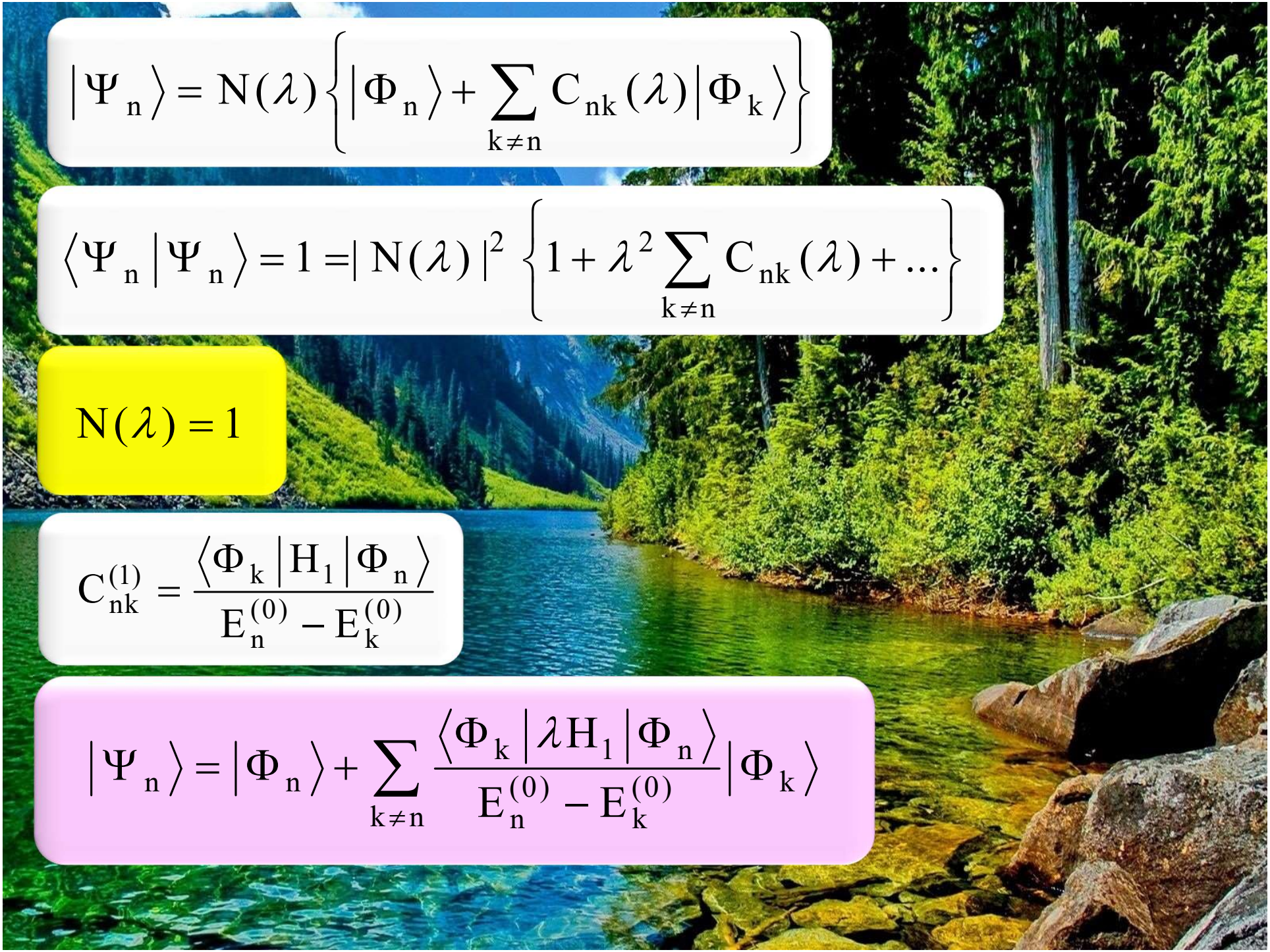
$$H_0\sum_{k\neq n}C_{nk}^{(2)}\left|\Phi_k\right\rangle+H_1\sum_{k\neq n}C_{nk}^{(1)}\left|\Phi_k\right\rangle=E_n^{(0)}\sum_{k\neq n}C_{nk}^{(2)}(\lambda)\left|\Phi_k\right\rangle+E_n^{(1)}\sum_{k\neq n}C_{nk}^{(1)}\left|\Phi_k\right\rangle+E_n^{(2)}\left|\Phi_n\right\rangle$$

$$E_n^{(2)}=\sum_{k\neq n}\left\langle\Phi_n\left|H_1\right|\Phi_k\right\rangle C_{nk}^{(1)}$$

$$C_{nk}^{(1)}=\frac{\left\langle\Phi_k\left|H_1\right|\Phi_n\right\rangle}{E_n^{(0)}-E_k^{(0)}}$$

$$E_n^{(2)}=\sum_{k\neq n}\frac{\left\langle\Phi_n\left|H_1\right|\Phi_k\right\rangle\left\langle\Phi_k\left|H_1\right|\Phi_n\right\rangle}{E_n^{(0)}-E_k^{(0)}}=\sum_{k\neq n}\frac{\left|\left\langle\Phi_k\left|H_1\right|\Phi_n\right\rangle\right|^2}{E_n^{(0)}-E_k^{(0)}}$$

$$E_n^{(2)}=\sum_{k\neq n}\frac{\left|\left\langle\Phi_k\left|H_1\right|\Phi_n\right\rangle\right|^2}{E_n^{(0)}-E_k^{(0)}}$$



$$|\Psi_n\rangle = N(\lambda)\left\{|\Phi_n\rangle + \sum_{k\neq n} C_{nk}(\lambda)|\Phi_k\rangle\right\}$$

$$\langle\Psi_n|\Psi_n\rangle = 1 = |N(\lambda)|^2\left\{1 + \lambda^2 \sum_{k\neq n} C_{nk}(\lambda) + \ldots\right\}$$

$$N(\lambda) = 1$$

$$C_{nk}^{(1)} = \frac{\langle\Phi_k|H_1|\Phi_n\rangle}{E_n^{(0)} - E_k^{(0)}}$$

$$|\Psi_n\rangle = |\Phi_n\rangle + \sum_{k\neq n} \frac{\langle\Phi_k|\lambda H_1|\Phi_n\rangle}{E_n^{(0)} - E_k^{(0)}}|\Phi_k\rangle$$

Example: calculate the energy shift up to first order in qε of a charged particle for which their Hamiltonian:

$$H = \frac{P^2}{2m} + \frac{1}{2} m\omega^2 x^2 + q\varepsilon x$$

$$H_0 = \frac{P^2}{2m} + \frac{1}{2} m\omega^2 x^2$$

$$H_1 = q\varepsilon x$$

$$E_n^{(1)} = \langle \Phi_n | H_1 | \Phi_n \rangle$$

$$E_n^{(1)} = \langle n | H_1 | n \rangle$$

$$q\varepsilon < n | x | n >$$

$$< n | x | n >= 0$$

Why?

$$A = \sqrt{\frac{m\omega}{2\hbar}}x + i\frac{p}{\sqrt{2m\omega\hbar}}$$

$$A^{\dagger} = \sqrt{\frac{m\omega}{2\hbar}}x - i\frac{p}{\sqrt{2m\omega\hbar}}$$

$$x = \sqrt{\frac{\hbar}{2m\omega}}\left(A + A^{\dagger}\right)$$

$$A\,|n> = \sqrt{n}\,|n-1>$$

$$A^{\dagger}\,|n> = \sqrt{n+1}\,|n+1>$$

$$<n|x|n> = \sqrt{n}\,<n|n-1> + \sqrt{n+1}\,<n+1|n>$$

$$<n|x|n> = 0 + 0 = 0$$

Or

$$\int_{-\infty}^{\infty} dx\; x\left|\Phi_n(x)\right|^2 \xrightarrow{\text{for Odd integrand}} 0$$

$$E_n^{(2)} = \sum_{k \neq n} \frac{\left|\langle \Phi_k | \lambda H_1 | \Phi_n \rangle\right|^2}{E_n^{(0)} - E_k^{(0)}}$$

$$H_1 = q\varepsilon x$$

$$E_n^{(2)} = q^2\varepsilon^2 \sum_{k \neq n} \frac{\left|\langle k | x | n \rangle\right|^2}{\hbar\omega(n-k)}$$

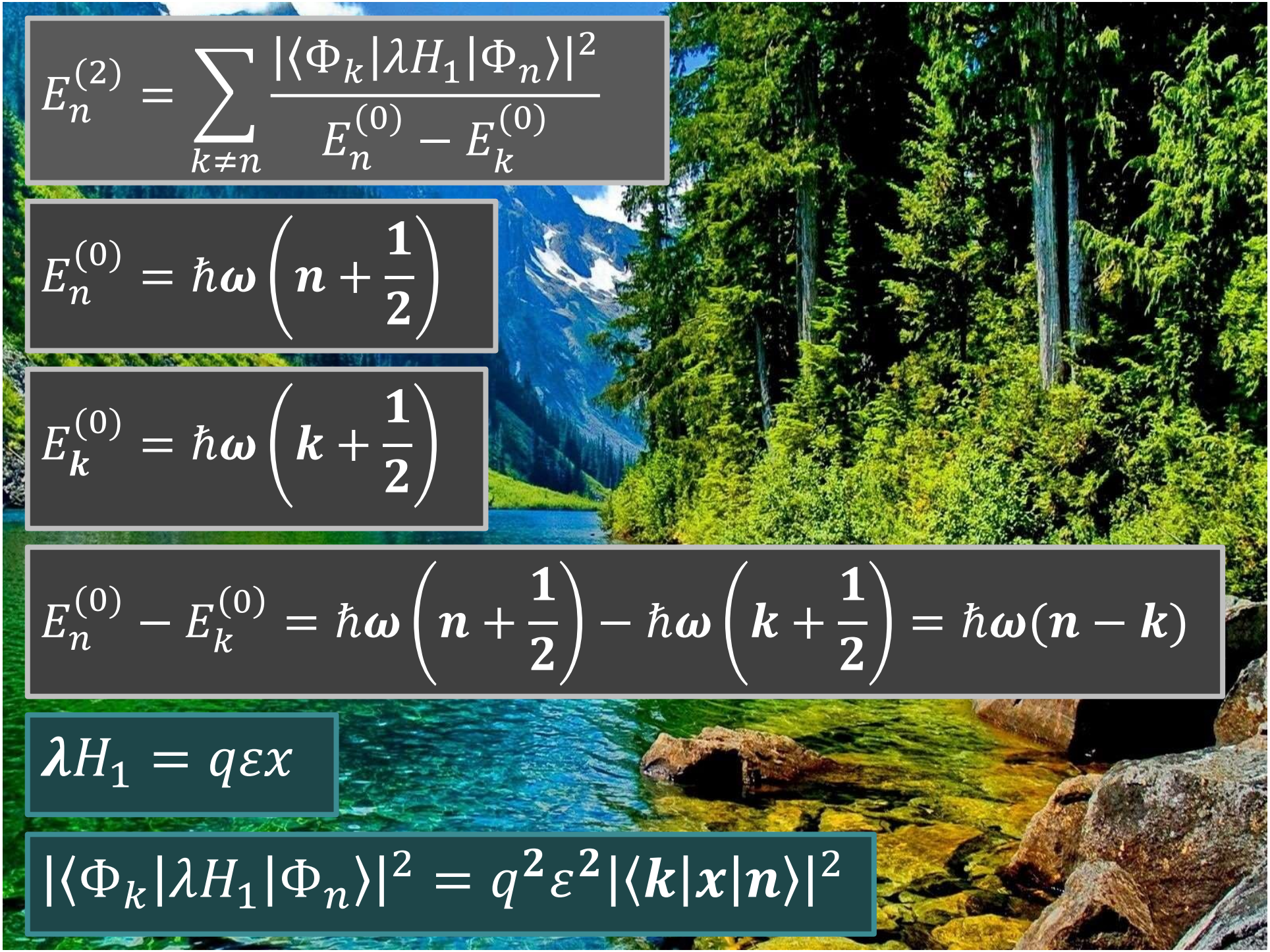
$$x = \sqrt{\frac{\hbar}{2m\omega}}\left(A + A^\dagger\right)$$

$$E_n^{(2)} = \frac{q^2\varepsilon^2}{2m\omega^2} \sum_{k \neq n} \frac{\left|\langle k | A + A^\dagger | n \rangle\right|^2}{n-k}$$

Only k=n-1 and k=n+1 terms are nonzero

$$E_n^{(2)} = \frac{q^2\varepsilon^2}{2m\omega^2}\left(\frac{\left|\sqrt{n}\right|^2}{1} + \frac{\left|\sqrt{n+1}\right|^2}{-1}\right) = -\frac{q^2\varepsilon^2}{2m\omega^2}$$

This result does not depend on n.



$$E_n^{(2)} = \sum_{k \neq n} \frac{|\langle \Phi_k | \lambda H_1 | \Phi_n \rangle|^2}{E_n^{(0)} - E_k^{(0)}}$$

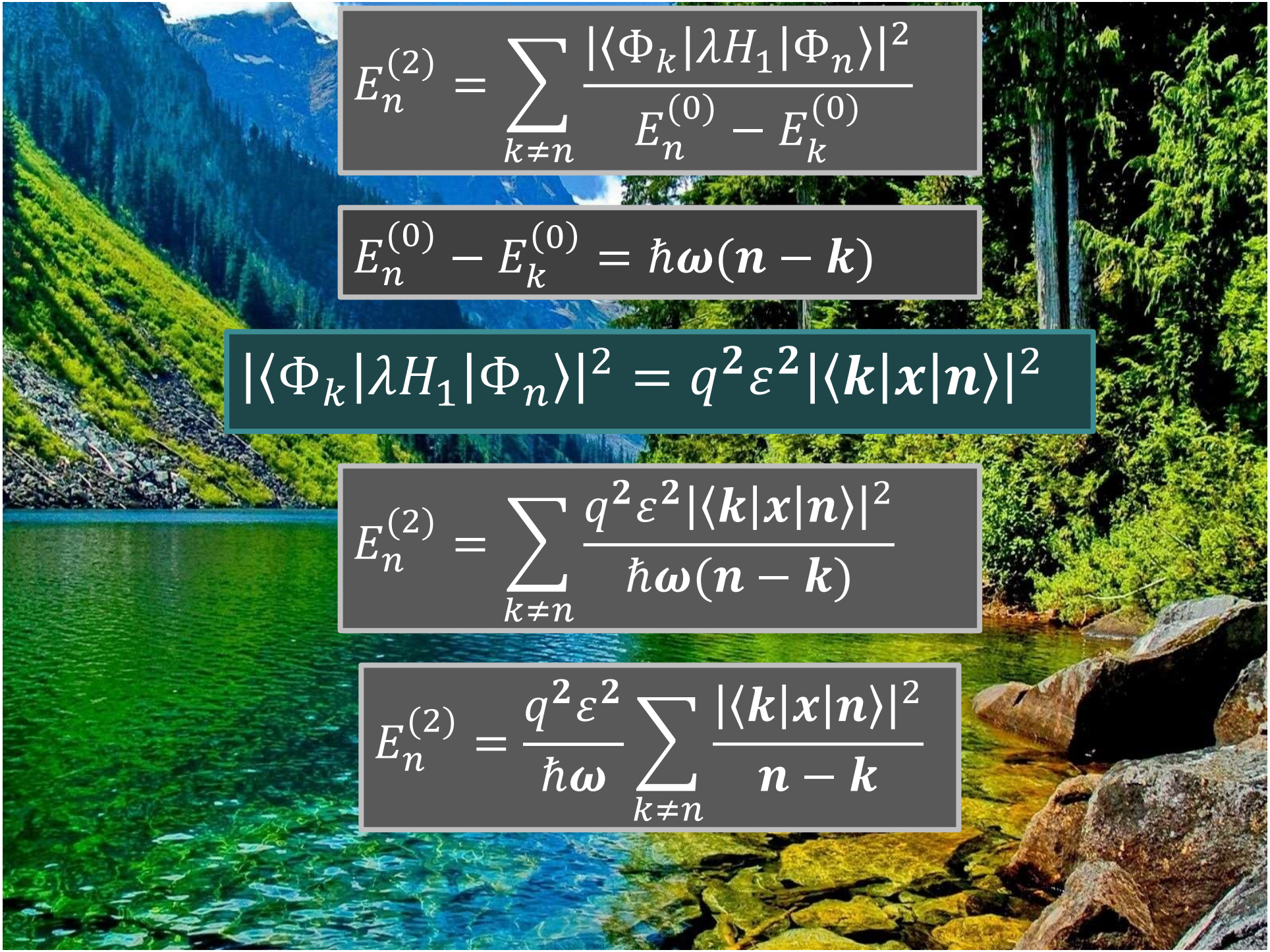
$$E_n^{(0)} = \hbar\omega\left(n + \frac{1}{2}\right)$$

$$E_k^{(0)} = \hbar\omega\left(k + \frac{1}{2}\right)$$

$$E_n^{(0)} - E_k^{(0)} = \hbar\omega\left(n + \frac{1}{2}\right) - \hbar\omega\left(k + \frac{1}{2}\right) = \hbar\omega(n - k)$$

$$\lambda H_1 = q\varepsilon x$$

$$|\langle \Phi_k | \lambda H_1 | \Phi_n \rangle|^2 = q^2\varepsilon^2 |\langle k | x | n \rangle|^2$$



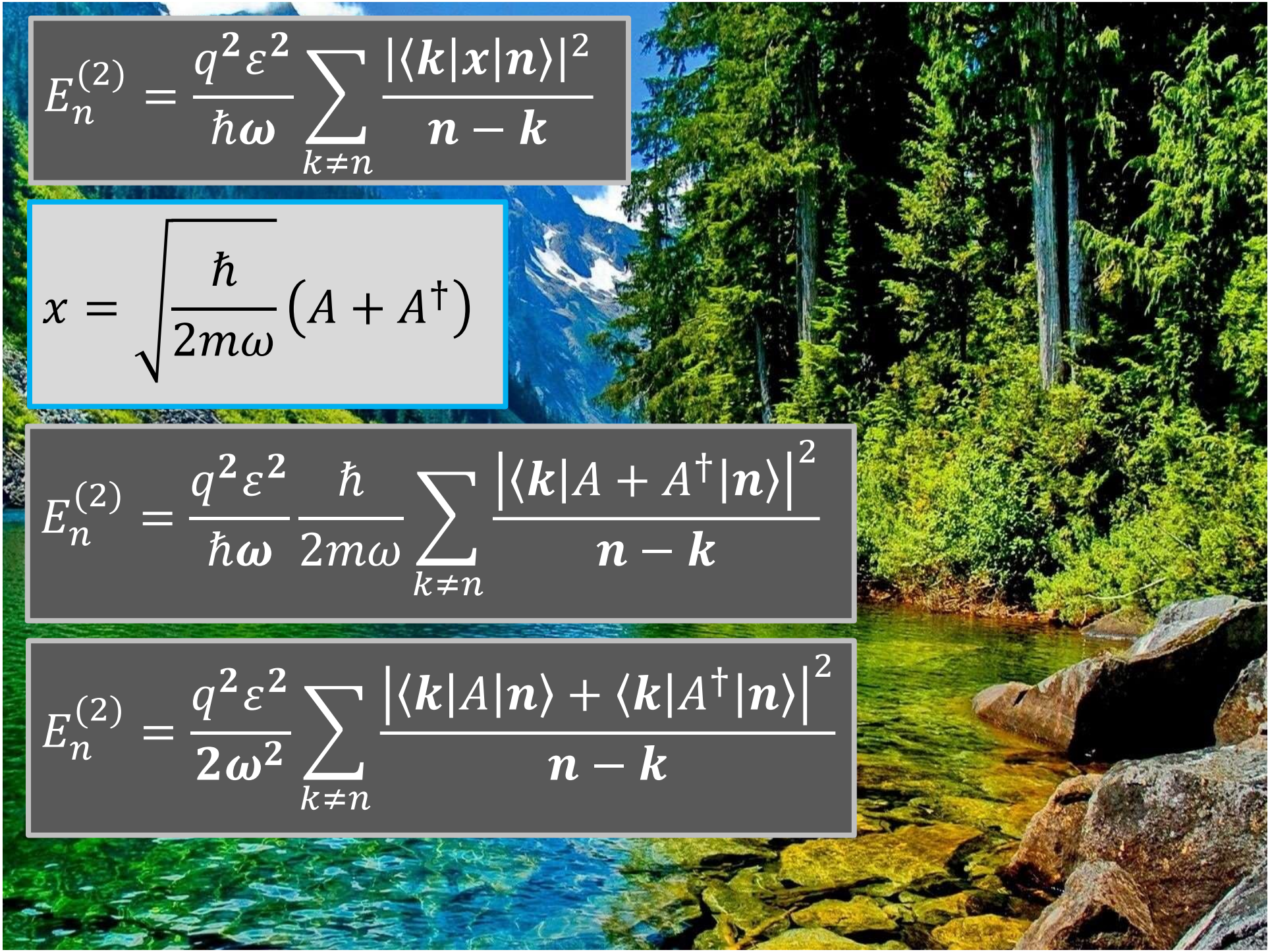
$$E_n^{(2)} = \sum_{k \neq n} \frac{|\langle \Phi_k | \lambda H_1 | \Phi_n \rangle|^2}{E_n^{(0)} - E_k^{(0)}}$$

$$E_n^{(0)} - E_k^{(0)} = \hbar\omega(n - k)$$

$$|\langle \Phi_k | \lambda H_1 | \Phi_n \rangle|^2 = q^2 \varepsilon^2 |\langle k | x | n \rangle|^2$$

$$E_n^{(2)} = \sum_{k \neq n} \frac{q^2 \varepsilon^2 |\langle k | x | n \rangle|^2}{\hbar\omega(n - k)}$$

$$E_n^{(2)} = \frac{q^2 \varepsilon^2}{\hbar\omega} \sum_{k \neq n} \frac{|\langle k | x | n \rangle|^2}{n - k}$$



$$E_n^{(2)} = \frac{q^2\varepsilon^2}{\hbar\omega}\sum_{k\neq n}\frac{|\langle k|x|n\rangle|^2}{n-k}$$

$$x = \sqrt{\frac{\hbar}{2m\omega}}\left(A + A^\dagger\right)$$

$$E_n^{(2)} = \frac{q^2\varepsilon^2}{\hbar\omega}\frac{\hbar}{2m\omega}\sum_{k\neq n}\frac{\left|\langle k|A + A^\dagger|n\rangle\right|^2}{n-k}$$

$$E_n^{(2)} = \frac{q^2\varepsilon^2}{2\omega^2}\sum_{k\neq n}\frac{\left|\langle k|A|n\rangle + \langle k|A^\dagger|n\rangle\right|^2}{n-k}$$

$$E_n^{(2)} = \frac{q^2\varepsilon^2}{2\omega^2} \sum_{k \neq n} \frac{\left|\langle k|A|n\rangle + \langle k|A^\dagger|n\rangle\right|^2}{n-k}$$

$$E_n^{(2)} = \frac{q^2\varepsilon^2}{2\omega^2} \sum_{k \neq n} \frac{\left|\sqrt{n}\langle k|n-1\rangle + \sqrt{n+1}\langle k|n+1\rangle\right|^2}{n-k}$$

$$E_n^{(2)} = \frac{q^2\varepsilon^2}{2\omega^2} \sum_{k \neq n} \frac{\left|\sqrt{n}\delta_{k,n-1} + \sqrt{n+1}\delta_{k,n+1}\right|^2}{n-k}$$

$$E_n^{(2)} = \frac{q^2\varepsilon^2}{2\omega^2} \sum_{k \neq n} \frac{n\left(\delta_{k,n-1}\right)^2 + (n+1)\left(\delta_{k,n+1}\right)^2 + 2\sqrt{n(n+1)}\delta_{k,n-1}\delta_{k,n+1}}{n-k}$$

$$E_n^{(2)} = \frac{q^2\varepsilon^2}{2\omega^2}\sum_{k\neq n}\frac{n\left(\delta_{k,n-1}\right)^2 + (n+1)\left(\delta_{k,n+1}\right)^2 + 2\sqrt{n(n+1)}\,\delta_{k,n-1}\delta_{k,n+1}}{n-k}$$

$$E_n^{(2)} = \frac{q^2\varepsilon^2}{2\omega^2}\left\{\sum_{k\neq n}\frac{n\left(\delta_{k,n-1}\right)^2}{n-k} + \sum_{k\neq n}\frac{(n+1)\left(\delta_{k,n+1}\right)^2}{n-k} + \sum_{k\neq n}\frac{2\sqrt{n(n+1)}\,\delta_{k,n-1}\delta_{k,n+1}}{n-k}\right\}$$

$$E_n^{(2)} = \frac{q^2\varepsilon^2}{2\omega^2}\left\{\sum_{k\neq n}\frac{n\delta_{k,n-1}}{n-k} + \sum_{k\neq n}\frac{(n+1)\delta_{k,n+1}}{n-k} + \sum_{k\neq n}\frac{2\sqrt{n(n+1)}\times 0}{n-k}\right\}$$

$$E_n^{(2)} = \frac{q^2\varepsilon^2}{2\omega^2}\left\{\frac{n}{n-(n-1)} + \frac{n+1}{n-(n+1)} + 0\right\}$$

$$E_n^{(2)} = \frac{q^2\varepsilon^2}{2\omega^2}\left\{\frac{n}{n-(n-1)} + \frac{n+1}{n-(n+1)} + 0\right\}$$

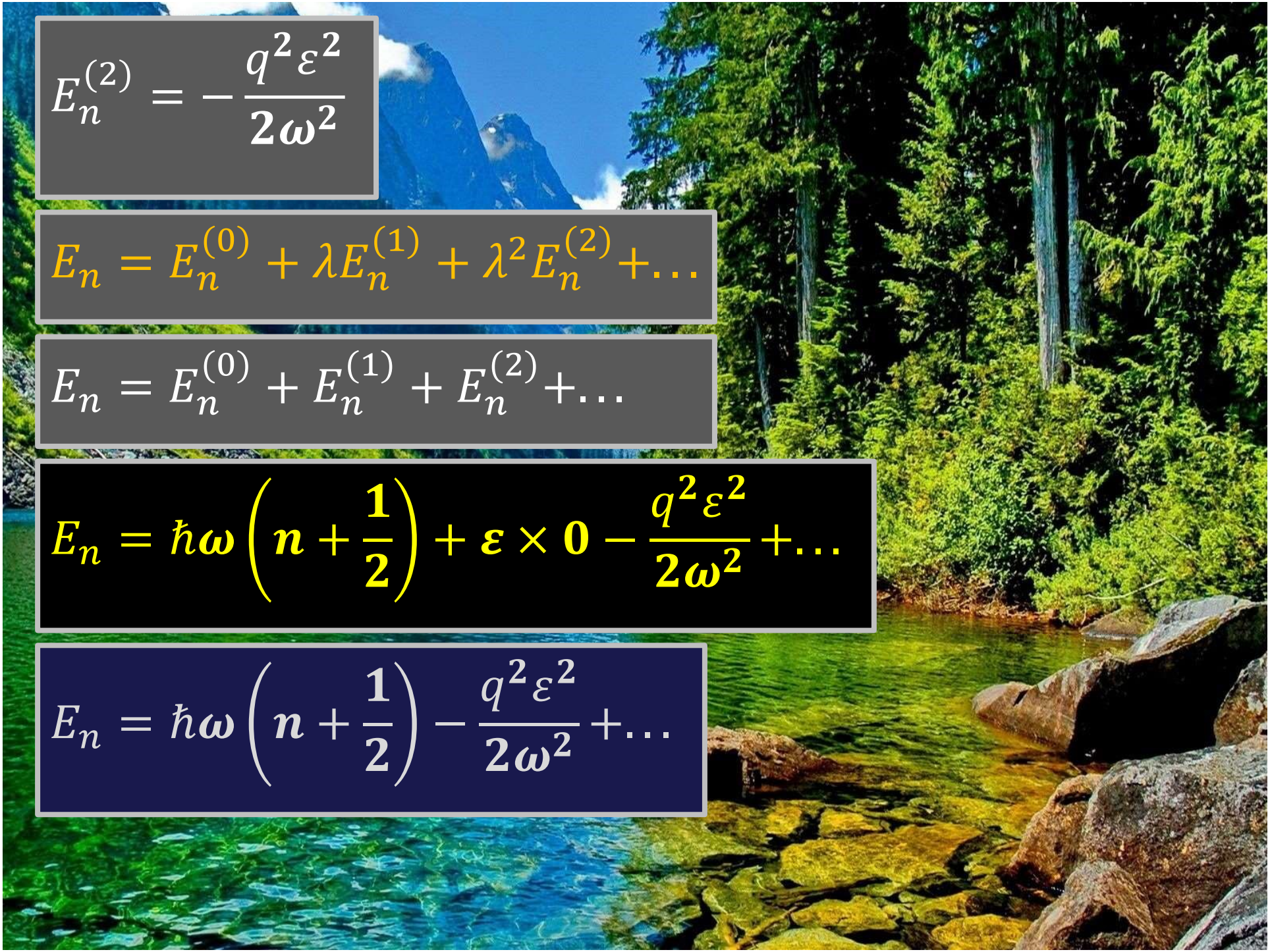
$$E_n^{(2)} = \frac{q^2\varepsilon^2}{2\omega^2}\left\{\frac{n}{1} + \frac{n+1}{-1}\right\}$$

$$E_n^{(2)} = \frac{q^2\varepsilon^2}{2\omega^2}\{n-n-1\}$$

$$E_n^{(2)} = \frac{q^2\varepsilon^2}{2\omega^2}\{-1\}$$

$$E_n^{(2)} = -\frac{q^2\varepsilon^2}{2\omega^2}$$

This result does not depend on n.



$$E_n^{(2)} = -\frac{q^2\varepsilon^2}{2\omega^2}$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots$$

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \ldots$$

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) + \varepsilon \times 0 - \frac{q^2\varepsilon^2}{2\omega^2} + \ldots$$

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) - \frac{q^2\varepsilon^2}{2\omega^2} + \ldots$$

Exact solution

$$\frac{1}{2}m\omega^2x^2+q\varepsilon x=\frac{1}{2}m\omega^2\left(x^2+\frac{2q\varepsilon}{m\omega^2}x\right)$$

$$=\frac{1}{2}m\omega^2\left(x+\frac{q\varepsilon}{m\omega^2}\right)^2-\frac{q^2\varepsilon^2}{2m\omega^2}$$

$$E_n^{(2)}=-\frac{q^2\varepsilon^2}{2m\omega^2}$$

Which is consistent with the result of the second order perturbation.

نظریه اختلال تبهگن

اگر هامیلتونی مختل نشده دو یا چند ویژه مقدار یکسان داشته باشد با مشکل خاصی رو به رو می شویم. معادله زیر

$$C_{nk}^{(1)} = \frac{\langle \Phi_k | H_1 | \Phi_n \rangle}{E_n^{(0)} - E_k^{(0)}}$$

نشان می دهد که به ازای مقادیری از n و k که به ازای آنها $E_n^{(0)}$ و $E_k^{(0)}$ برابر می شوند $C_{nk}^{(1)}$ بینهایت می شود.

چنین مواردی زمانی رخ می دهد که ویژه مقادیر هامیلتونی H_0 تبهگن باشند.

روش کلی این است که نخست تبهگنی را از بین برد و سپس مانند سابق عمل کرد.

به عنوان مثال برای یک ماتریس 3×3 این کار را انجام می دهیم.

فرض می کنیم که $E_1^{(0)} = E_2^{(0)} = E^{(0)}$ باشد. در این صورت خواهیم داشت:

$$H_0 = \begin{pmatrix} E^{(0)} & 0 & 0 \\ 0 & E^{(0)} & 0 \\ 0 & 0 & E_3^{(0)} \end{pmatrix}$$

$$\lambda H_1 = \begin{pmatrix} \lambda h_{11} & \lambda h_{12} & \lambda h_{13} \\ \lambda h_{21} & \lambda h_{22} & \lambda h_{23} \\ \lambda h_{31} & \lambda h_{32} & \lambda h_{33} \end{pmatrix}$$

مشروط بر این که شرط هرمیتی بودن برقرار باشد:

$$h_{ij} = h_{ji}^*$$

اینک مساله را به دو قسمت تفکیک می کنیم:

نخست ماتریس 2×2 گوشه بالایی سمت چپ را قطری می کنیم.

$$\lambda H_1 = \begin{pmatrix} \lambda h_{11} & \lambda h_{12} & \lambda h_{13} \\ \lambda h_{21} & \lambda h_{22} & \lambda h_{23} \\ \lambda h_{31} & \lambda h_{32} & \lambda h_{33} \end{pmatrix}$$

چنانچه قبلا گفتیم هر ماتریس هرمیتی **H** با تبدیل یکانی **U** قطری می شود:

$$UHU^{\dagger} = H_D$$

ماتریس یکانی ای که فقط به بلوک 2×2 گوشه بالایی سمت چپ اثر کند به شکل زیر خواهد بود:

$$U = \begin{pmatrix} \times & \times & 0 \\ \times & \times & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

که در آن ×ها U_{ij} های نامعلوم را نمایش می دهند.

آنچه که مهم است این است که این **U** بر H_0 اثری ندارد، زیرا:

گوشه پایین سمت راست در 1 ضرب می شود و گوشه 2×2 سمت چپ H_0 به شکل $E^{(0)}\times I_{2\times2}$ است.

چون $UI_{2\times2}U^{+}=I_{2\times2}$ است، از این رو این گوشه تغییر نمی کند.

$$UH_0U^{\dagger}=\begin{pmatrix}\times & \times & 0\\ \times & \times & 0\\ 0 & 0 & 1\end{pmatrix}\begin{pmatrix}E^{(0)} & 0 & 0\\ 0 & E^{(0)} & 0\\ 0 & 0 & E_3^{(0)}\end{pmatrix}\begin{pmatrix}\times & \times & 0\\ \times & \times & 0\\ 0 & 0 & 1\end{pmatrix}$$

دقت کنید که اینها نماد × می باشند نه نماد **X**. این بدان معنی است که اعداد مجهول × در مکانهای مختلف می تواند با هم متفاوت باشند.

$$=\begin{pmatrix}E^{(0)} & 0 & 0\\ 0 & E^{(0)} & 0\\ 0 & 0 & E_3^{(0)}\end{pmatrix}$$

بنابراین اثر خالص قطری کردن این است که ماتریس 2×2 زیر

$$\begin{pmatrix} \lambda h_{11} & \lambda h_{12} \\ \lambda h_{21} & \lambda h_{22} \end{pmatrix}$$

قطری کنیم.

محاسبه مقادیر ویژه ماتریس 2×2 آسان است.

$$\det\begin{pmatrix} \lambda h_{11} - \lambda\omega & \lambda h_{12} \\ \lambda h_{21} & \lambda h_{22} - \lambda\omega \end{pmatrix} = 0$$

$$(\lambda h_{11} - \lambda\omega)(\lambda h_{22} - \lambda\omega) - \lambda^2 h_{12} h_{21} = 0$$

$$\lambda^2 h_{11} h_{22} - \lambda^2 h_{11}\omega - \lambda^2 h_{22}\omega + \lambda^2\omega^2 - \lambda^2 h_{12} h_{21} = 0$$

$$\omega^2 - (h_{11} + h_{22})\omega + h_{11} h_{22} - h_{12} h_{21} = 0$$

$$\omega = \frac{h_{11} + h_{22} \pm \sqrt{(h_{11} + h_{22})^2 - 4h_{11}h_{22} + 4h_{12}h_{21}}}{2}$$

$$\omega = \frac{h_{11} + h_{22} \pm \sqrt{(h_{11} + h_{22})^2 - 4h_{11}h_{22} + 4h_{12}h_{21}}}{2}$$

$$\omega = \frac{h_{11} + h_{22} \pm \sqrt{h_{11}^2 + h_{22}^2 + 2h_{11}h_{22} - 4h_{11}h_{22} + 4h_{12}h_{21}}}{2}$$

$$\omega = \frac{h_{11} + h_{22} \pm \sqrt{h_{11}^2 + h_{22}^2 - 2h_{11}h_{22} + 4h_{12}h_{21}}}{2}$$

$$\omega = \frac{h_{11} + h_{22} \pm \sqrt{(h_{11} - h_{22})^2 + 4h_{12}h_{21}}}{2}$$

$$\omega = \frac{h_{11} + h_{22} \pm \sqrt{(h_{11} - h_{22})^2 + 4h_{12}h_{21}}}{2}$$

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$$\omega = \frac{h_{11} + h_{22}}{2} \pm \sqrt{\frac{(h_{11} - h_{22})^2 + 4h_{12}h_{21}}{\mathbf{4}}}$$

$$\omega = \frac{h_{11} + h_{22}}{2} \pm \sqrt{\frac{(h_{11} - h_{22})^2}{4} + \frac{4h_{12}h_{21}}{4}}$$

$$\omega_{1,2} = \frac{h_{11} + h_{22}}{2} \pm \sqrt{\left(\frac{h_{11} - h_{22}}{2}\right)^2 + h_{12}h_{21}}$$

$$H = H_0 + \lambda H_1$$

$$UHU^\dagger = UH_0U^\dagger + \lambda UH_1U^\dagger$$

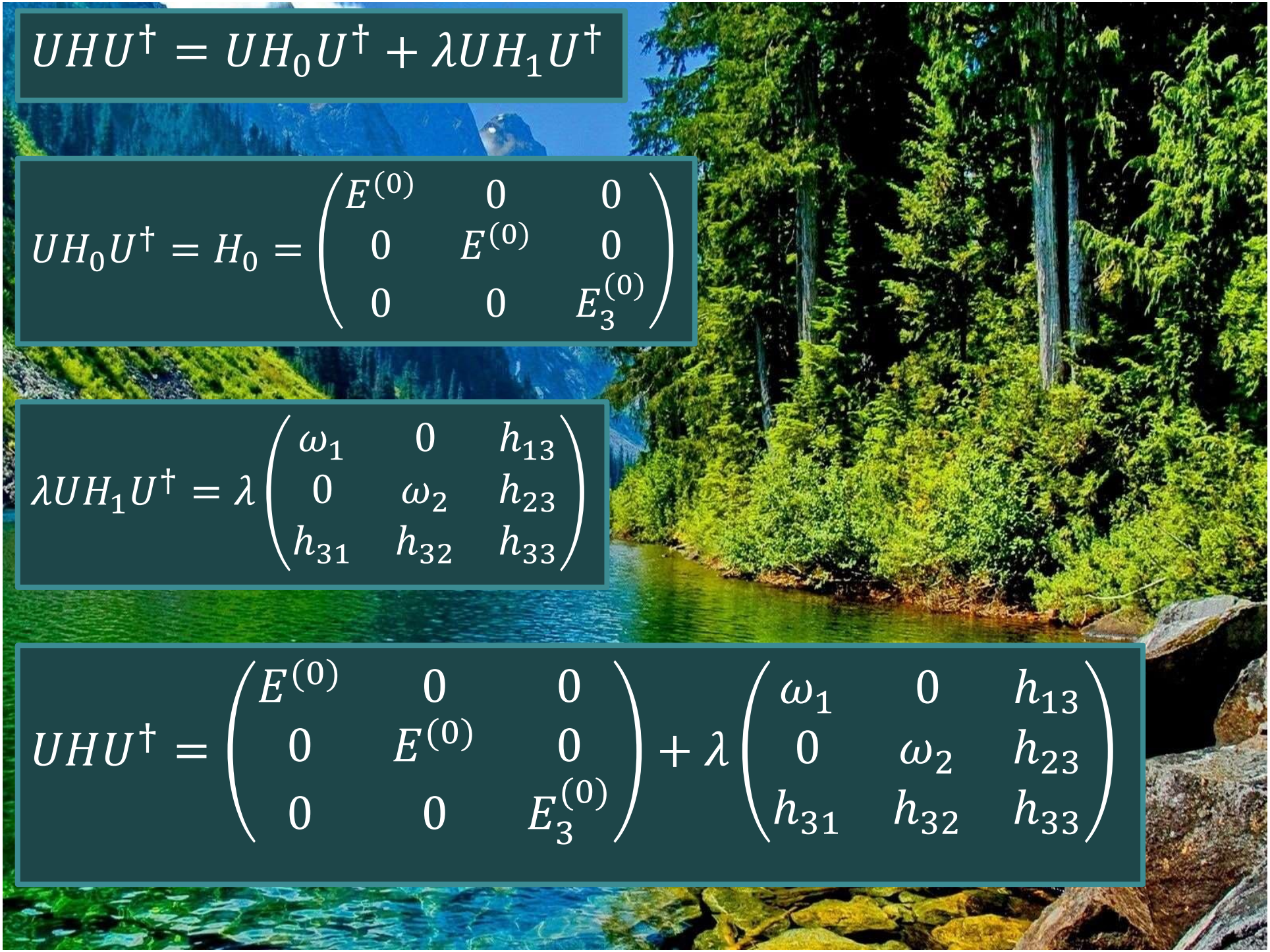
$$U = \begin{pmatrix} \times & \times & 0 \\ \times & \times & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$H_0 = \begin{pmatrix} E^{(0)} & 0 & 0 \\ 0 & E^{(0)} & 0 \\ 0 & 0 & E_3^{(0)} \end{pmatrix}$$

$$\lambda H_1 = \lambda \begin{pmatrix} h_{11} & h_{12} & h_{13} \\ h_{21} & h_{22} & h_{23} \\ h_{31} & h_{32} & h_{33} \end{pmatrix}$$

$$UH_0U^\dagger = H_0 = \begin{pmatrix} E^{(0)} & 0 & 0 \\ 0 & E^{(0)} & 0 \\ 0 & 0 & E_3^{(0)} \end{pmatrix}$$

$$\lambda UH_1U^\dagger = \lambda \begin{pmatrix} \omega_1 & 0 & h_{13} \\ 0 & \omega_2 & h_{23} \\ h_{31} & h_{32} & h_{33} \end{pmatrix}$$



$$UHU^{\dagger} = UH_0U^{\dagger} + \lambda UH_1U^{\dagger}$$

$$UH_0U^{\dagger} = H_0 = \begin{pmatrix} E^{(0)} & 0 & 0 \\ 0 & E^{(0)} & 0 \\ 0 & 0 & E_3^{(0)} \end{pmatrix}$$

$$\lambda UH_1U^{\dagger} = \lambda \begin{pmatrix} \omega_1 & 0 & h_{13} \\ 0 & \omega_2 & h_{23} \\ h_{31} & h_{32} & h_{33} \end{pmatrix}$$

$$UHU^{\dagger} = \begin{pmatrix} E^{(0)} & 0 & 0 \\ 0 & E^{(0)} & 0 \\ 0 & 0 & E_3^{(0)} \end{pmatrix} + \lambda \begin{pmatrix} \omega_1 & 0 & h_{13} \\ 0 & \omega_2 & h_{23} \\ h_{31} & h_{32} & h_{33} \end{pmatrix}$$

$$UHU^{\dagger} = \begin{pmatrix} E^{(0)} & 0 & 0 \\ 0 & E^{(0)} & 0 \\ 0 & 0 & E_3^{(0)} \end{pmatrix} + \lambda \begin{pmatrix} \omega_1 & 0 & h_{13} \\ 0 & \omega_2 & h_{23} \\ h_{31} & h_{32} & h_{33} \end{pmatrix}$$

$$UHU^{\dagger} = \begin{pmatrix} E^{(0)} + \lambda\omega_1 & 0 & \lambda h_{13} \\ 0 & E^{(0)} + \lambda\omega_2 & \lambda h_{23} \\ \lambda h_{31} & \lambda h_{32} & E_3^{(0)} + h_{33} \end{pmatrix}$$

$$UHU^{\dagger} = \begin{pmatrix} E^{(0)} + \lambda\omega_1 & 0 & 0 \\ 0 & E^{(0)} + \lambda\omega_2 & 0 \\ 0 & 0 & E_3^{(0)} \end{pmatrix} + \lambda \begin{pmatrix} 0 & 0 & h_{13} \\ 0 & 0 & h_{23} \\ h_{31} & h_{32} & h_{33} \end{pmatrix}$$

بنابراین پس از قطری کردن ماتریس کل به شکل زیر در می آید:

$$H = \begin{pmatrix} E^{(0)} + \lambda\omega_1 & 0 & \lambda h_{13} \\ 0 & E^{(0)} + \lambda\omega_2 & \lambda h_{23} \\ \lambda h_{31} & \lambda h_{32} & E_3^{(0)} + \lambda h_{33} \end{pmatrix}$$

که در آن:

$$\omega_{1,2} = \frac{h_{11} + h_{22}}{2} \pm \sqrt{\left(\frac{h_{11} - h_{22}}{2}\right)^2 + h_{12}h_{21}}$$

حال تبهگنی را برداشته ایم و می توانیم فرمولهایی را که در نظریه اختلال غیر تبهگن به دست آورده بودیم بدون هیچ گونه مشکلی بکار ببریم.

اگر با ماتریس 5×5 شروع می کردیم و سه ویژه مقدار H_0 با هم برابر بودند، آنگاه باید زیر ماتریس 3×3 از ماتریس λH_1 را قطری می کردیم که انجام آن دردسردارد ولی اصول فرقی نمی کند.

به همین منوال اگر در مثال 3×3 قبلی هر سه ویژه مقدار H_0 با هم برابر بودند، آنگاه مجبور بودیم ماتریس 3×3ی λH_1 را قطری کنیم که جوابهای دقیق به دست می آمد چون در این صورت خود H قطری می شد.

بحث نظریه اختلال تبهگن را بیش از این پی می گیریم:

در نظریه اختلال تبهگن مساله این است که به جای یک $|\Phi_n>$ منحصربه فرد مجموعه ای متناهی از $|\Phi_n^{(i)}>$ ها وجود دارد که جملگی انرژی یکسانی مانند $E_n^{(0)}$ دارند.

این مجموعه را می توان نسبت به برچسب i راستهنجار کرد، زیرا چنانچه در بخش قبل دیدیم این برچسب می تواند با ویژه مقادیر برخی از عملگرهای هرمیتی جابه جا شونده وابسته باشد.

از این رو مجموعه $|\Phi_n^{(i)}>$ را چنان اختیار می کنیم که:

$$\left\langle \Phi_m^{(i)} \middle| \Phi_n^{(j)} \right\rangle = \delta_{mn}\delta_{ij}$$

در نظریه اختلال غیر تبهگن داشتیم که:

$$|\Psi_n\rangle = N(\lambda)\left\{|\Phi_n\rangle + \sum_{k\neq n} C_{nk}(\lambda)|\Phi_k\rangle\right\}$$

حال در نظریه اختلال تبهگن راه طبیعی منظور کردن تبهگنی این است که تابع موج $|\psi_n\rangle$ را با عبارتی شامل ترکیبهای خطی از ویژه توابع تبهگن H_0 جایگزین کنیم:

$$|\Psi_n\rangle = N(\lambda)\left\{\sum_i \alpha_i |\Phi_n^{(i)}\rangle + \lambda \sum_{k\neq n} C_{nk}^{(1)} \sum_i \beta_i |\Phi_k^{(i)}\rangle + \ldots\right\}$$

ضرایب α_i، β_i و ... را باید تعیین کنیم.

$$\left|\Psi_n\right\rangle = N(\lambda)\left\{\sum_i \alpha_i \left|\Phi_n^{(i)}\right\rangle + \lambda \sum_{k\neq n} C_{nk}^{(1)} \sum_i \beta_i \left|\Phi_k^{(i)}\right\rangle + \ldots\right\}$$

اگر رابطه فوق را در معادله شرودینگر قرار دهیم:

$$H|\Psi_n\rangle = E_n|\Psi_n\rangle$$

$$H = H_0 + \lambda H_1$$

$$H_0\left|\Phi_n\right\rangle = E_n^{(0)}\left|\Phi_n\right\rangle$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots$$

$$(H_0+\lambda H_1)|\Psi_n\rangle=(H_0+\lambda H_1)N(\lambda)\left\{\sum_i \alpha_i\left|\Phi_n^{(i)}\right\rangle+\lambda\sum_{k\neq n}C_{nk}^{(1)}\sum_i\beta_i\left|\Phi_k^{(i)}\right\rangle+\ldots\right\}$$

$$=\left(E_n^{(0)}+\lambda E_n^{(1)}+\cdots\right)N(\lambda)\left\{\sum_i \alpha_i\left|\Phi_n^{(i)}\right\rangle+\lambda\sum_{k\neq n}C_{nk}^{(1)}\sum_i\beta_i\left|\Phi_k^{(i)}\right\rangle+\ldots\right\}$$

$$N(\lambda)\lambda\left[H_0\sum_{k\neq n}C_{nk}^{(1)}\sum_i\beta_i\left|\Phi_k^{(i)}\right\rangle+H_1\sum_i\alpha_i\left|\Phi_n^{(i)}\right\rangle\right]=N(\lambda)\lambda\left[E_n^{(0)}\sum_{k\neq n}C_{nk}^{(1)}\sum_i\beta_i\left|\Phi_k^{(i)}\right\rangle+E_n^{(1)}\sum_i\alpha_i\left|\Phi_n^{(i)}\right\rangle\right]$$

$$H_0\sum_{k\neq n}C_{nk}^{(1)}\sum_i\beta_i\left|\Phi_k^{(i)}\right\rangle+H_1\sum_i\alpha_i\left|\Phi_n^{(i)}\right\rangle=E_n^{(0)}\sum_{k\neq n}C_{nk}^{(1)}\sum_i\beta_i\left|\Phi_k^{(i)}\right\rangle+E_n^{(1)}\sum_i\alpha_i\left|\Phi_n^{(i)}\right\rangle$$

حاصل ضرب نرده ای این معادله با $\langle\Phi_n^{(j)}|$ معادله جا به جایی مرتبه اول را می دهد:

$$\sum_i \alpha_i\left\langle\Phi_n^{(j)}\right|H_1\left|\Phi_n^{(i)}\right\rangle=\alpha_j E_n^{(1)}$$

$$\sum_i \alpha_i \left\langle \Phi_n^{(j)} \middle| H_1 \middle| \Phi_n^{(i)} \right\rangle = \alpha_j E_n^{(1)}$$

یک مساله ویژه مقدار با ابعاد متناهی است.

مثلا چنانچه تبهگنی دوگانه وجود داشته باشد و اگر از نماد گذاری زیر استفاده کنیم:

$$\left\langle \Phi_n^{(j)} \middle| H_1 \middle| \Phi_n^{(i)} \right\rangle = h_{ji}$$

آنگاه معادله ویژه مقدار فوق را می توان به صورت زیر نوشت:

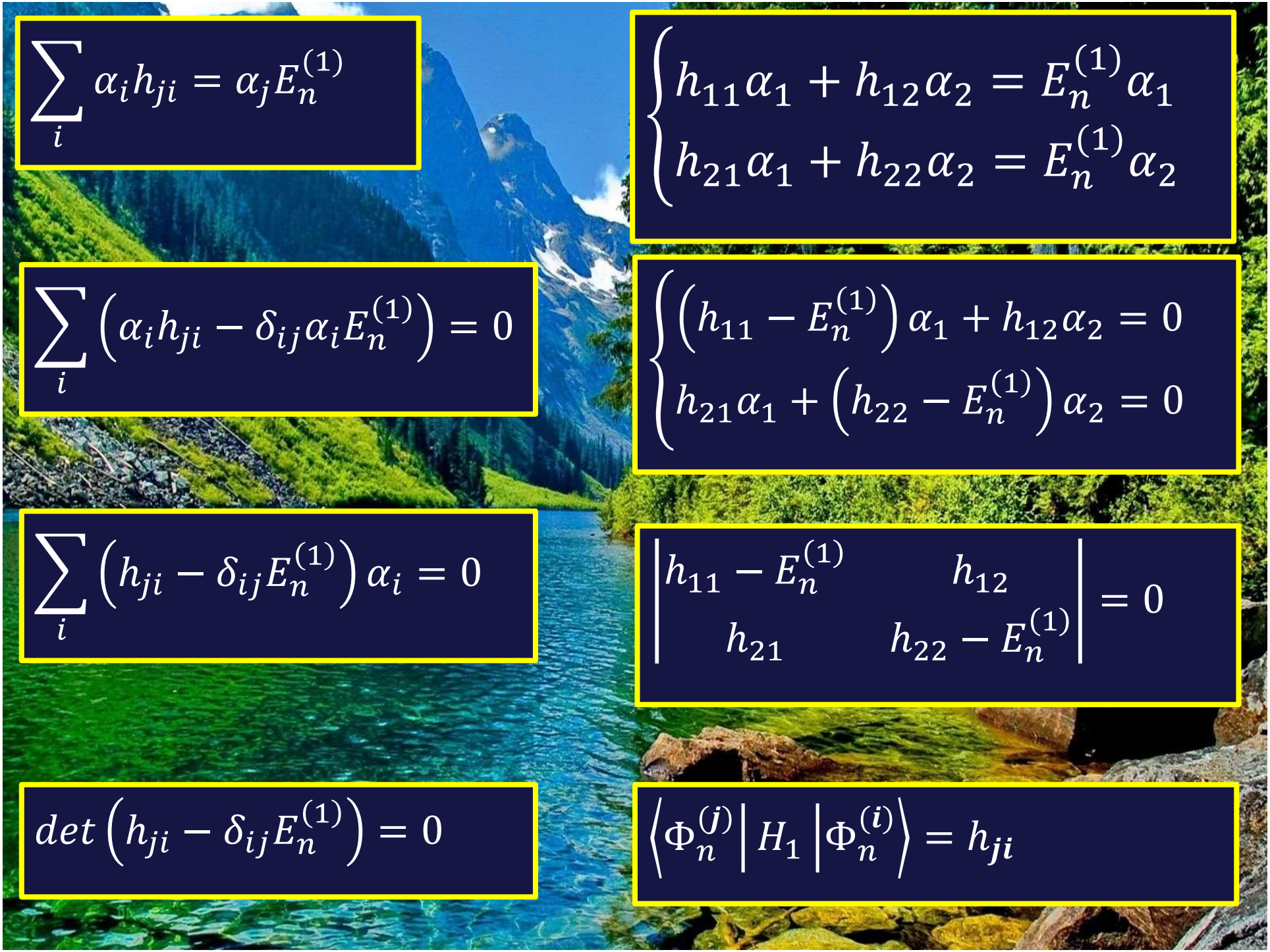
$$\sum_i \alpha_i h_{ji} = \alpha_j E_n^{(1)}$$

ویژه مقادیر $E_n^{(1)}$ و ویژه حالتهای α_i را می توان از این معادله تعین کرد مشروط بر این که شرط زیر

$$\sum_i |\alpha_i|^2 = 1$$

را اضافه کنیم.

$$\begin{cases} h_{11}\alpha_1 + h_{12}\alpha_2 = E_n^{(1)}\alpha_1 \\ h_{21}\alpha_1 + h_{22}\alpha_2 = E_n^{(1)}\alpha_2 \end{cases}$$



$$\sum_i \alpha_i h_{ji} = \alpha_j E_n^{(1)}$$

$$\begin{cases} h_{11}\alpha_1 + h_{12}\alpha_2 = E_n^{(1)}\alpha_1 \\ h_{21}\alpha_1 + h_{22}\alpha_2 = E_n^{(1)}\alpha_2 \end{cases}$$

$$\sum_i \left(\alpha_i h_{ji} - \delta_{ij}\alpha_i E_n^{(1)}\right) = 0$$

$$\begin{cases} \left(h_{11} - E_n^{(1)}\right)\alpha_1 + h_{12}\alpha_2 = 0 \\ h_{21}\alpha_1 + \left(h_{22} - E_n^{(1)}\right)\alpha_2 = 0 \end{cases}$$

$$\sum_i \left(h_{ji} - \delta_{ij}E_n^{(1)}\right)\alpha_i = 0$$

$$\begin{vmatrix} h_{11} - E_n^{(1)} & h_{12} \\ h_{21} & h_{22} - E_n^{(1)} \end{vmatrix} = 0$$

$$det\left(h_{ji} - \delta_{ij}E_n^{(1)}\right) = 0$$

$$\left\langle \Phi_n^{(j)} \middle| H_1 \middle| \Phi_n^{(i)} \right\rangle = h_{ji}$$

تمرین: ویژه حالتهای β_i را تعیین کنید.

راهنمایی: از رابطه زیر شروع کنید و ضرایب متناظر را در دوطرف معادله مساوی هم قرار دهید و انرژی اختلال تبهگن را هم تا مرتبه دوم به دست آورید.

$$(H_0+\lambda H_1)|\Psi_n\rangle = (H_0+\lambda H_1)N(\lambda)\left\{\sum_i \alpha_i \left|\Phi_n^{(i)}\right\rangle + \lambda \sum_{k\neq n} C_{nk}^{(1)} \sum_i \beta_i \left|\Phi_k^{(i)}\right\rangle + \ldots\right\}$$

$$= \left(E_n = E_n^{(0)} + \lambda E_n^{(1)} + \cdots\right) N(\lambda)\left\{\sum_i \alpha_i \left|\Phi_n^{(i)}\right\rangle + \lambda \sum_{k\neq n} C_{nk}^{(1)} \sum_i \beta_i \left|\Phi_k^{(i)}\right\rangle + \ldots\right\}$$

$$\sum_i \alpha_i h_{ji} = \alpha_j E_n^{(1)}$$

چنانچه به ازای $i \neq j$ داشته باشیم $h_{ij}=0$، یعنی ماتریس قطری باشد، آنگاه عناصر قطری این ماتریس همان جابه جایی های مرتبه اول خواهند بود.

چنین اتفاقی زمانی روی می دهد که اختلال H_1 با عملگری جابه جا شود که ویژه مقادیرش را برچسبهای i نمایش می دهند.

برای مثال تبهگنی در اتم هیدروژن با ویژه مقادیر L_z وابسته است، یعنی همه مقادیر m انرژی یکسانی دارند.

اگر بر حسب اتفاق داشته باشیم که:

$$[H_1, L_z] = 0$$

و اگر $|\Phi_n^{(j)}>$ را ویژه توابع عملگر L_z انتخاب کنیم، آنگاه h_{ij} قطری خواهد بود.

$$L_z \left|\Phi_n^{(i)}\right\rangle = \hbar m^{(i)} \left|\Phi_n^{(i)}\right\rangle$$

برای اثبات به صورت زیر عمل می کنیم:

$$0 = \left\langle \Phi_n^{(j)} \middle| [H_1, L_z] \middle| \Phi_n^{(i)} \right\rangle = \left\langle \Phi_n^{(j)} \middle| H_1 L_z - L_z H_1 \middle| \Phi_n^{(i)} \right\rangle$$

$$0 = \hbar m^{(i)} \left\langle \Phi_n^{(j)} \middle| H_1 \middle| \Phi_n^{(i)} \right\rangle - \hbar m^{(j)} \left\langle \Phi_n^{(j)} \middle| H_1 \middle| \Phi_n^{(i)} \right\rangle$$

$$\mathbf{0} = \hbar\left(m^{(i)} - m^{(j)}\right) h_{ji}$$

$$m^{(i)} - m^{(j)} \neq 0 \Rightarrow h_{ji} = 0$$

برای مثال چرخنده صلبی که با هامیلتونی زیر

$$H_0 = \frac{L^2}{2I}$$

توصیف شده است، دارای گشتاور مغناطیسی کوچک زیر می باشد:

$$\mu = \frac{qg}{2M}\mathbf{L}$$

این چرخنده را در یک میدان مغناطیسی در راستای **z** قرار می دهیم.

در این صورت هامیلتونی اختلال به شکل زیر می باشد:

$$H_1 = -\frac{qg}{2M}BL_z$$

چون ویژه توابع H_0 عبارت اند از Y_{lm} که ویژه توابع همزمان L_z نیز هستند

پس می توانیم ویژه مقادیر را به آسانی پیدا کنیم:

$$E = \frac{l(l+1)\hbar^2}{2I} - \frac{qgB\hbar}{2M} m_l; \quad -l \le m_l \le l$$

در فصل بعد که اتم هیدروین واقعی را شرح خواهیم داد و مثالهای دیگری را خواهیم دید.

اثر استارک

برای نشان دادن کاربرد نظریه اختلال در یک مساله واقعی اثر میدان الکتریکی را روی ترازهای اتم هیدروژن گونه در نظر می گیریم.

این اثر را اثر استارک می گویند.

هامیلتونی مختل نشده چنین است:

$$H_0 = \frac{p^2}{2\mu} - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

که ویژه توابع آن را با Φ_{nlm} نشان می دهیم.

پتانسیل اختلال چنین است:

$$\lambda H_1 = e\boldsymbol{\varepsilon}.\mathbf{r} = e\varepsilon z$$

$$\lambda = e\varepsilon$$

جابه جایی انرژی حالت پایه که تنهگن نیست برابر است با:

$$E_{100}^{(1)} = e\varepsilon \langle \Phi_{100} | z | \Phi_{100} \rangle = e\varepsilon \int d^3 r |\Phi_{100}|^2 z = 0$$

این انتگرال صفر می شود چون مجذور تابع موج تخت همیشه دارای پاریته مثبت است و پتانسیل اختلال تحت بازتاب تابع فردی است.

بنابراین حالت پایه هیچ جابه جایی انرژی ندارد که نسبت به میدان الکتریکی خطی باشد.

در فیزیک کلاسیک هر دستگاهی که گشتاور دوقطبی الکتریکی d داشته باشد یک جابه جایی انرژی به بزرگی $d.\varepsilon$ - را تجربه خواهد کرد.

اگر هامیلتونی مختل نشده تحت بازتاب ناوردا باشد می توان استدلال پاریته را چنین تعمیم داد:

دستگاه هایی که در حالتهای تبهگن نباشند نمی توانند گشتاورهای دو قطبی دایمی داشته باشند.

عبارت تبهگن نبودن مهم است چون فقط در این شرایط است که حالتها ویژه حالتهای عملگر پاریته نیز هستند و مربع اندازه تابع موج مثبت است و بنابراین مقدار چشمداشتی z صفر می شود.

ملکول هایی هستند که گشتاورهای دو قطبی دایمی دارند چون این ملکولهاحالتهای پایه تبهگنی با پاریته مخالف دارند.

اگر این حالتها را با $|\psi_+>$ و $|\psi_->$ نمایش دهیم آنگاه مقدار چمداشتی z در حالتی مثل $\alpha |\psi_+> + \beta |\psi_->$ صفر نخواهد شد:

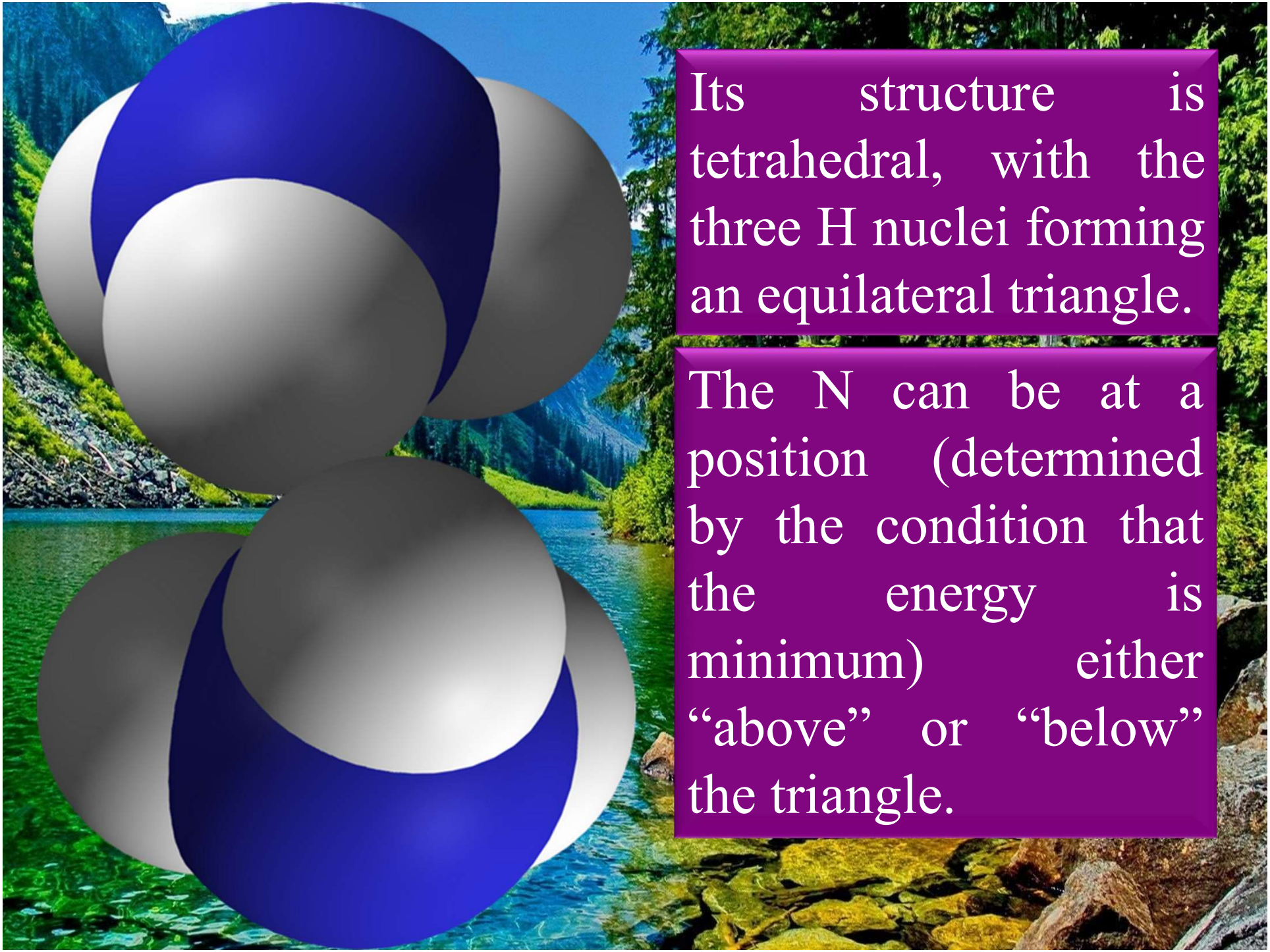
$$\langle \alpha\Psi_+ + \beta\Psi_- | z | \alpha\Psi_+ + \beta\Psi_- \rangle =$$
$$= \alpha^* \beta \langle \Psi_+ | z | \Psi_- \rangle + \alpha\beta^* \langle \Psi_- | z | \Psi_+ \rangle \neq 0$$

پس شرط تبهگن نبودن برای صفر شدن شیفت تا مرتبه اول لازم است.

This explanation is not quite correct.

The reason is that the lowest-lying states are never quite degenerate.

Consider, for example, a molecule like ammonia, NH_3:



Its structure is tetrahedral, with the three H nuclei forming an equilateral triangle.

The N can be at a position (determined by the condition that the energy is minimum) either “above” or “below” the triangle.

The even and odd linear combinations of these two states do not have quite the same energy, though the energy difference is very tiny (-10^{-4}eV) because of the large barrier between the "above" and "below" locations.

Thus, strictly speaking, the ground state is nondegenerate.

However (as we shall see soon), if εd, where

$$d = e\int \Psi^*_{\text{above}} z \Psi_{\text{below}} d^3r = -e\int \Psi^*_{\text{below}} z \Psi_{\text{above}} d^3r$$

is much larger than the tiny splitting, then the energy shift will be linear in the electric field, and the molecule will behave as if it had an electric dipole moment.

Let us look at the second term.

It reads

$$E_{100}^{(2)} = e^2 \varepsilon^2 \sum_{nlm} \frac{\left| \langle \Phi_{nlm} | z | \Phi_{100} \rangle \right|^2}{E_1^{(0)} - E_n^{(0)}}$$

The matrix element in this expression is

$$\langle \Phi_{nlm} | z | \Phi_{100} \rangle = \int d^3 r R_{nlm}(r) Y_{lm}^*(\theta, \varphi) r \cos\theta R_{100}(r) Y_{00}(\theta, \varphi)$$

Where we have replaced z by the more convenient rcosθ.

The angular part of the integration can be carried out, since

$$\cos\theta = \sqrt{\frac{4\pi}{3}} Y_{10}$$

$$Y_{00} = \sqrt{\frac{1}{4\pi}}$$

It is therefore

$$\int d\Omega Y_{lm}^{*}(\theta,\varphi)\frac{1}{\sqrt{3}}Y_{10}(\theta,\varphi) = \frac{1}{\sqrt{3}}\delta_{l1}\delta_{m0}$$

by the orthonormality of the Y_{lm}.

The fact that the m-value must be the same for the two states is our first example of a selection rule, which can be stated in the form $\Delta m=0$

It follows from the fact that

$$[L_z, z] = 0$$

that is, the perturbation commute with L_z.

One has to evaluate the radial integral to obtain the answer:

$$R = \int_0^\infty r^2 dr R_{n10}(r) r R_{100}(r)$$

Practice: evaluate the above integral using the radial functions of hydrogen atom.

If you do the practice, you will find the final result as follows:

$$\left|\left\langle \Phi_{n\ell m} \left| z \right| \Phi_{100} \right\rangle\right|^2 = \frac{1}{3}\frac{2^8 n^7 (n-1)^{2n-5}}{(n+1)^{2n+5}} a_0^2 = f(n) a_0^2$$

which we write as $f(n)a_0^2$.

For the second order shift, this gives

$$E_{100}^{(2)} = -e^2 \varepsilon^2 a_0^2 \sum_{n=2}^{\infty} \frac{f(n)}{\frac{1}{2}\mu^2 c^2 \alpha^2 \left(1 - \frac{1}{n^2}\right)}$$

$$E_{100}^{(2)} = -\frac{2e^2 \varepsilon^2 a_0^2}{\mu^2 c^2 \alpha^2} \sum_{n=2}^{\infty} \frac{n^2 f(n)}{n^2 - 1} = -2a_0^3 \varepsilon^2 \sum_{n=2}^{\infty} \frac{n^2 f(n)}{n^2 - 1}$$

On the face of it, the sum can only be evaluated term by term.

The n=2 term contributes 0.74 to the series, and the n=3 term contributes 0.1.

$$d = -\frac{\partial E_{100}^{(2)}}{\partial \varepsilon} = 4a_0^3 \varepsilon \sum_{n=2}^{\infty} \frac{n^2 f(n)}{n^2 - 1}$$

This is proportional to the electric field strength

The polarizibility, defined by

$$\chi_\varepsilon = \frac{d}{\varepsilon}$$

can thus be calculated.

$$\chi_\varepsilon = 4a_0^3 \sum_{n=2}^{\infty} \frac{n^2 f(n)}{n^2 - 1}$$

In making estimates of sums of the sort that occur in

$$E_{100}^{(2)} = e^2 \varepsilon^2 \sum_{nlm} \frac{\left| \langle \Phi_{nlm} | z | \Phi_{100} \rangle \right|^2}{E_1^{(0)} - E_n^{(0)}}$$

one may sometimes find useful upper bounds.

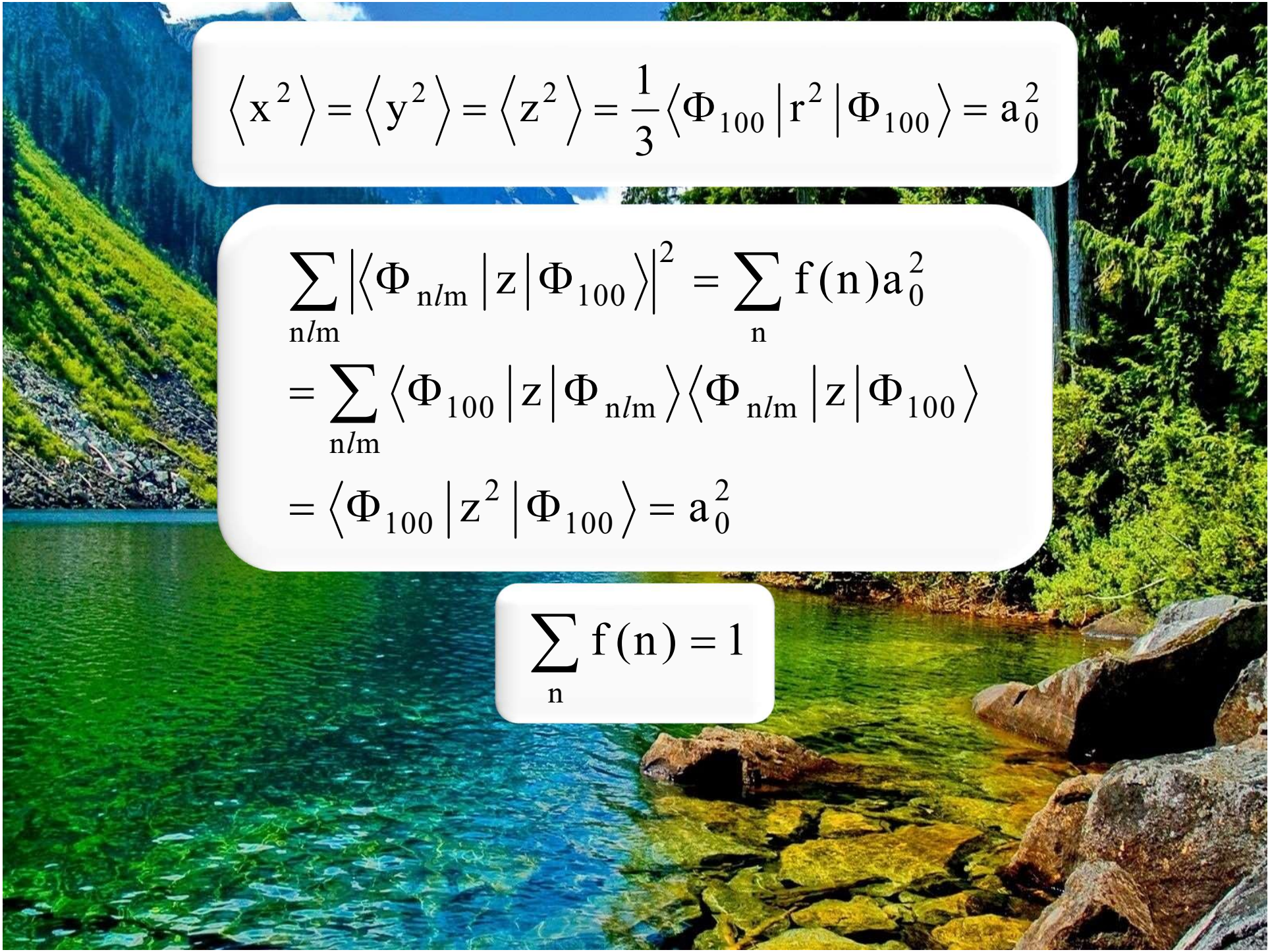
$$\sum_{nlm} \frac{\langle \Phi_{100} | z | \Phi_{nlm} \rangle \langle \Phi_{nlm} | z | \Phi_{100} \rangle}{E_1^{(0)} - E_n^{(0)}} <$$

$$\frac{1}{E_1^{(0)} - E_2^{(0)}} \sum_{nlm} \langle \Phi_{100} | z | \Phi_{nlm} \rangle \langle \Phi_{nlm} | z | \Phi_{100} \rangle$$

$$\sum_{nlm} |\Phi_{nlm}\rangle\langle\Phi_{nlm}| \longrightarrow 1$$

However, because of the completeness of the states, we may replace

$$\sum_{nlm} \frac{\langle \Phi_{100} | z | \Phi_{nlm} \rangle \langle \Phi_{nlm} | z | \Phi_{100} \rangle}{E_1^{(0)} - E_n^{(0)}} < \frac{\langle \Phi_{100} | z^2 | \Phi_{100} \rangle}{E_1^{(0)} - E_2^{(0)}}$$



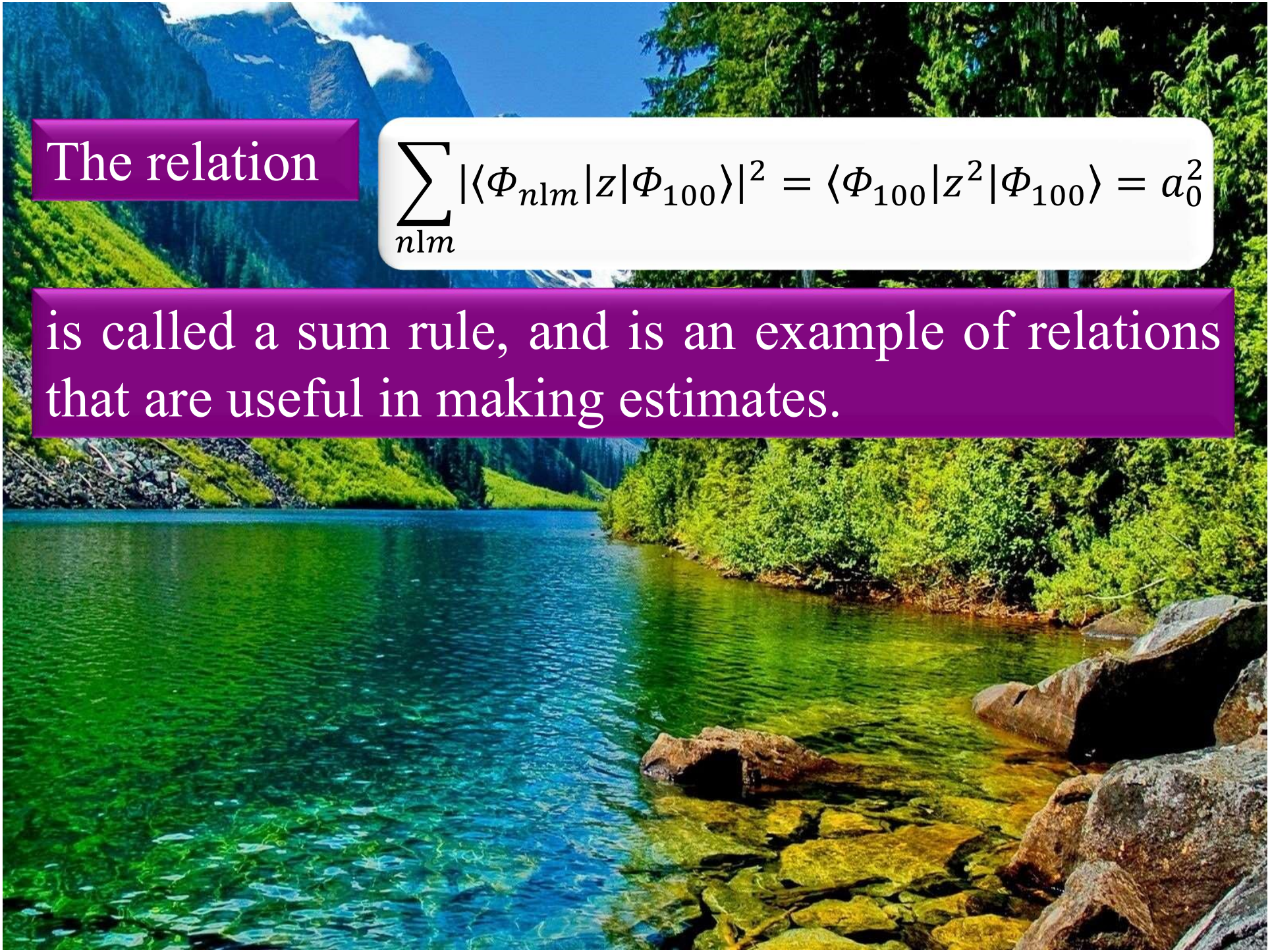
$$\left\langle x^2 \right\rangle = \left\langle y^2 \right\rangle = \left\langle z^2 \right\rangle = \frac{1}{3}\left\langle \Phi_{100} \left| r^2 \right| \Phi_{100} \right\rangle = a_0^2$$

$$\sum_{nlm} \left| \left\langle \Phi_{nlm} \left| z \right| \Phi_{100} \right\rangle \right|^2 = \sum_{n} f(n) a_0^2$$

$$= \sum_{nlm} \left\langle \Phi_{100} \left| z \right| \Phi_{nlm} \right\rangle \left\langle \Phi_{nlm} \left| z \right| \Phi_{100} \right\rangle$$

$$= \left\langle \Phi_{100} \left| z^2 \right| \Phi_{100} \right\rangle = a_0^2$$

$$\sum_{n} f(n) = 1$$


The relation
$\sum_{nlm} |\langle \Phi_{nlm}|z|\Phi_{100}\rangle|^2 = \langle \Phi_{100}|z^2|\Phi_{100}\rangle = a_0^2$
is called a sum rule, and is an example of relations that are useful in making estimates.

To illustrate degenerate perturbation theory, we calculate the first order (linear in ε) stark effect for the n=2 states of the hydrogen atom.

For the unperturbed system there are really four n=2 states that have the same energy.

These are

$$\Phi_{200} = (2a_0)^{-3/2}\, 2\left(1-\frac{r}{2a_0}\right) e^{-\frac{r}{2a_0}} Y_{00}$$

$$\Phi_{211} = (2a_0)^{-3/2}\, 3^{-1/2}\left(\frac{r}{a_0}\right) e^{-\frac{r}{2a_0}} Y_{11}$$

$$\Phi_{210} = (2a_0)^{-3/2}\, 3^{-1/2} \left(\frac{r}{a_0}\right) e^{-\frac{r}{2a_0}} Y_{10}$$

$$\Phi_{21,-1} = (2a_0)^{-3/2}\, 3^{-1/2} \left(\frac{r}{a_0}\right) e^{-\frac{r}{2a_0}} Y_{1,-1}$$

The l=0 state has even parity, and the l=1 states have odd parity.

We want to solve an equation like

$$\sum_i \alpha_i \left\langle \Phi_n^{(j)} \middle| H_1 \middle| \Phi_n^{(i)} \right\rangle = \alpha_j E_n^{(1)}$$

and on the face of it, four equations are involved.

$$\begin{aligned}\langle 200 \mid \hat{Z} \mid 210\rangle &= \int_0^\infty R_{20}^*(r) R_{21}(r) r^2 dr \int Y_{00}^*(\Omega) z\, Y_{10}(\Omega)\, d\Omega \\ &= \sqrt{\frac{4\pi}{3}} \int_0^\infty R_{20}(r) R_{21}(r) r^3 dr \int Y_{00}^*(\Omega) Y_{10}^2(\Omega)\, d\Omega \\ &= -3a_0 \end{aligned} \tag{9.59}$$

since $z = r\cos\theta = \sqrt{4\pi/3}\, r Y_{10}(\Omega)$, $\langle \vec{r} \mid 200\rangle = R_{20}(r) Y_{00}(\Omega)$, $\langle \vec{r} \mid 210\rangle = R_{21}(r) Y_{10}(\Omega)$, and $d\Omega = \sin\theta\, d\theta d\varphi$; $a_0 = \hbar^2/(\mu e^2)$ is the Bohr radius. The matrix of $\langle 2l'm' \mid \hat{H}_p \mid 2lm\rangle$ is

$$\begin{pmatrix} \langle 1 \mid \hat{H}_p \mid 1\rangle & \langle 1 \mid \hat{H}_p \mid 2\rangle & \langle 1 \mid \hat{H}_p \mid 3\rangle & \langle 1 \mid \hat{H}_p \mid 4\rangle \\ \langle 2 \mid \hat{H}_p \mid 1\rangle & \langle 2 \mid \hat{H}_p \mid 2\rangle & \langle 2 \mid \hat{H}_p \mid 3\rangle & \langle 2 \mid \hat{H}_p \mid 4\rangle \\ \langle 3 \mid \hat{H}_p \mid 1\rangle & \langle 3 \mid \hat{H}_p \mid 2\rangle & \langle 3 \mid \hat{H}_p \mid 3\rangle & \langle 3 \mid \hat{H}_p \mid 4\rangle \\ \langle 4 \mid \hat{H}_p \mid 1\rangle & \langle 4 \mid \hat{H}_p \mid 2\rangle & \langle 4 \mid \hat{H}_p \mid 3\rangle & \langle 4 \mid \hat{H}_p \mid 4\rangle \end{pmatrix} = -3e\mathcal{E}a_0 \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \tag{9.60}$$

where we have used the notation $\mid 1\rangle = \mid 200\rangle$, $\mid 2\rangle = \mid 211\rangle$, $\mid 3\rangle = \mid 210\rangle$, and $\mid 4\rangle = \mid 21-1\rangle$. Diagonalization of this matrix leads to the following eigenvalues:

$$E_2^{(1)}{}_1 = -3e\mathcal{E}a_0, \qquad E_2^{(1)}{}_2 = E_2^{(1)}{}_4 = 0, \qquad E_2^{(1)}{}_4 = 3e\mathcal{E}a_0. \tag{9.61}$$

Thus, the energy levels of the $n = 2$ states are given to first order by

$$E_{2_1} = -\frac{R_y}{4} - 3e\mathcal{E}a_0, \quad E_{2_2} = E_{2_3} = -\frac{R_y}{4} \quad E_{2_4} = -\frac{R_y}{4} + 3e\mathcal{E}a_0. \tag{9.62}$$

The corresponding eigenvectors to zeroth order are

$$|\,\psi_2\rangle_1 = \frac{1}{\sqrt{2}}\left(|\,200\rangle + |\,210\rangle\right), \qquad |\,\psi_2\rangle_2 = |\,211\rangle, \tag{9.63}$$

$$|\,\psi_2\rangle_3 = |\,21-1\rangle, \qquad |\,\psi_2\rangle_4 = \frac{1}{\sqrt{2}}\left(|\,200\rangle - |\,210\rangle\right). \tag{9.64}$$

This perturbation has only partially removed the degeneracy of the $n = 2$ level; the states $|\,211\rangle$ and $|\,21-1\rangle$ still have the same energy $E_3 = E_4 = -R_y/4$.

If we note, however, that

(a) the perturbation potential (that is, z) commutes with L_z so that it only connects states with the same m-value, and

(b) parity forces us to consider only terms in which the perturbation potential must connect l=1 to l=0 terms, that is

$$\left\langle \Phi_{2,1,\pm 1} \middle| z \middle| \Phi_{2,1,\pm 1} \right\rangle = 0$$

then the matrix in

is only a 2×2 matrix.

The equation reads

$$\sum_i \alpha_i \left\langle \Phi_n^{(j)} \middle| H_1 \middle| \Phi_n^{(i)} \right\rangle = \alpha_j E_n^{(1)}$$

$$e\varepsilon \begin{pmatrix} \langle \Phi_{200} | z | \Phi_{200} \rangle & \langle \Phi_{200} | z | \Phi_{210} \rangle \\ \langle \Phi_{210} | z | \Phi_{200} \rangle & \langle \Phi_{210} | z | \Phi_{210} \rangle \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} = E^{(1)} \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix}$$

The diagonal elements are zero, because of parity, and off-diagonal elements are equal, since they are complex conjugate of each other, and each may be chosen to be real.

We have

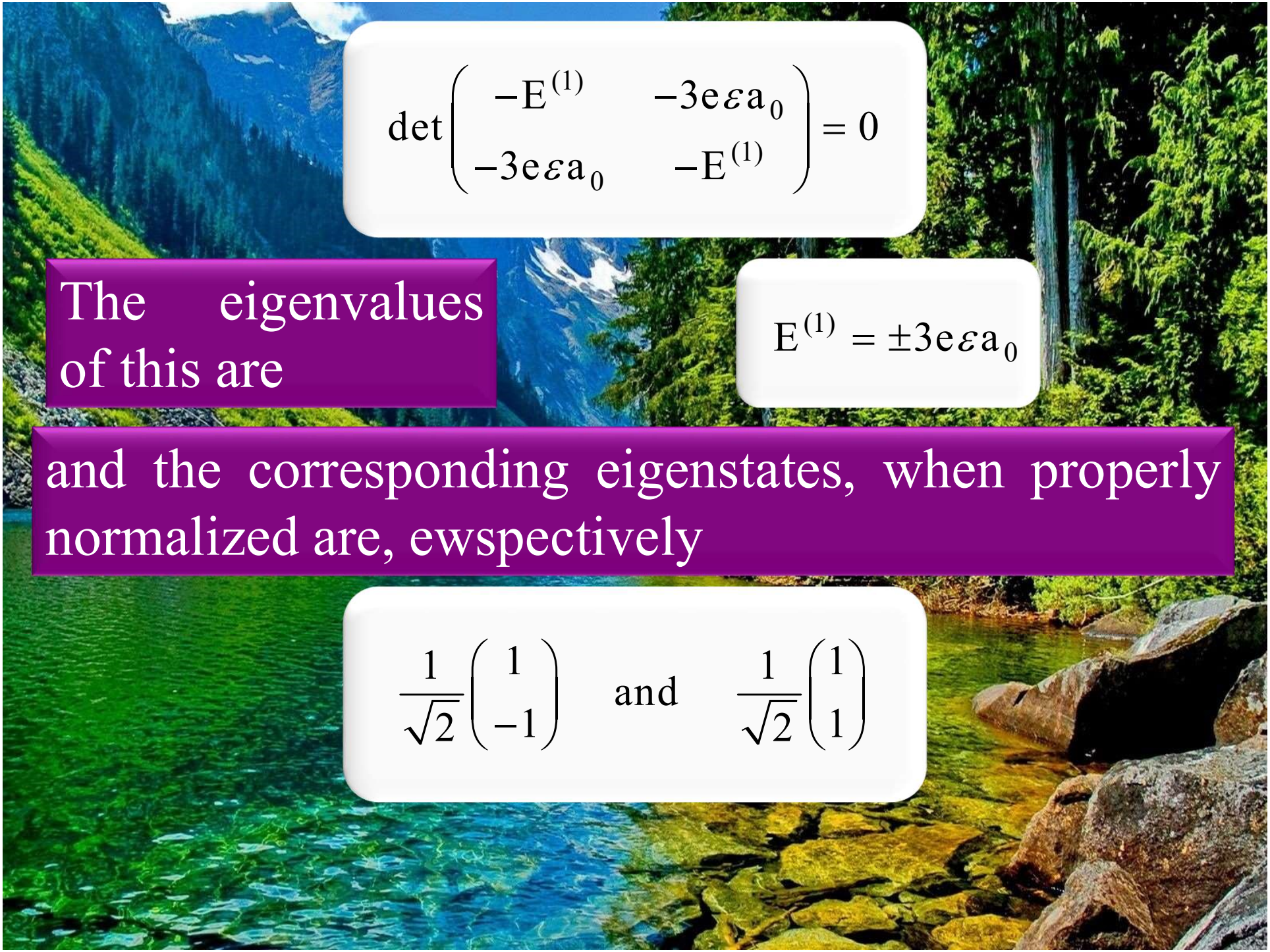
$$\left\langle \Phi_{200} \mid z \mid \Phi_{210} \right\rangle = \int_0^\infty r^2 dr \left(2a_0\right)^{-3} e^{-r/a_0} \frac{2r}{\sqrt{3}a_0}\left(1-\frac{r}{2a_0}\right) r$$

$$\times \int d\Omega Y_{00}^* \left(\sqrt{\frac{4\pi}{3}} Y_{10}\right) Y_{10} = -3a_0$$

and hence we have

$$e\varepsilon \begin{pmatrix} 0 & -3a_0 \\ -3a_0 & 0 \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} = E^{(1)} \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix}$$

$$\begin{pmatrix} -E^{(1)} & -3e\varepsilon a_0 \\ -3e\varepsilon a_0 & -E^{(1)} \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} = 0$$



$$\det\begin{pmatrix} -E^{(1)} & -3e\varepsilon a_0 \\ -3e\varepsilon a_0 & -E^{(1)} \end{pmatrix} = 0$$

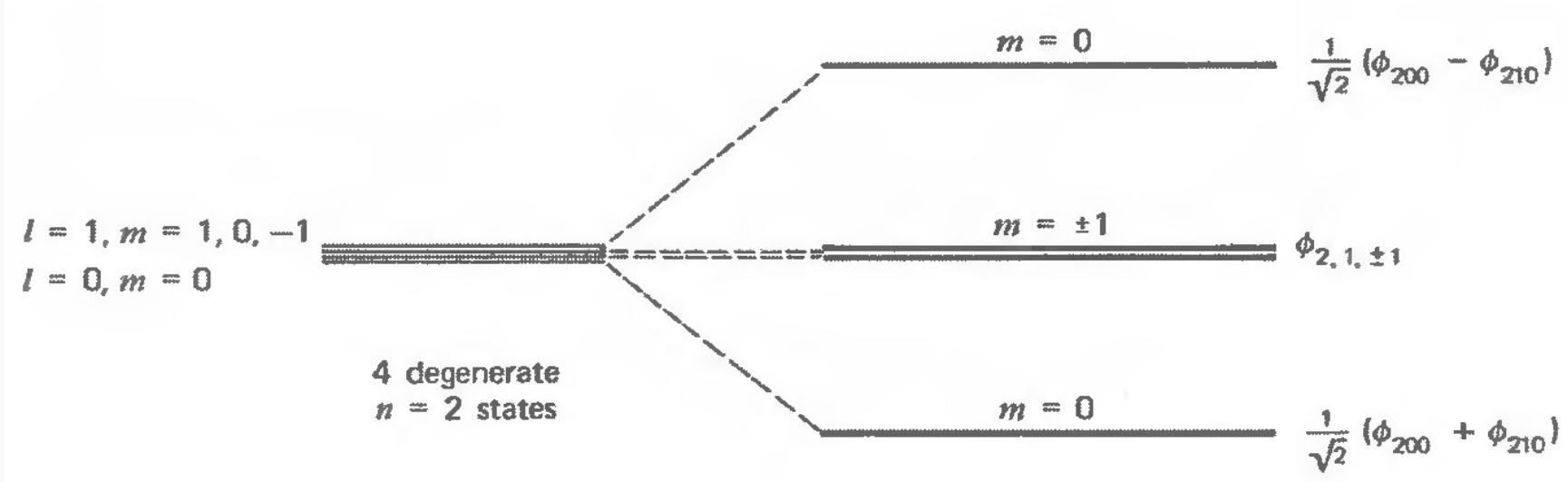
The eigenvalues of this are

$$E^{(1)} = \pm 3e\varepsilon a_0$$

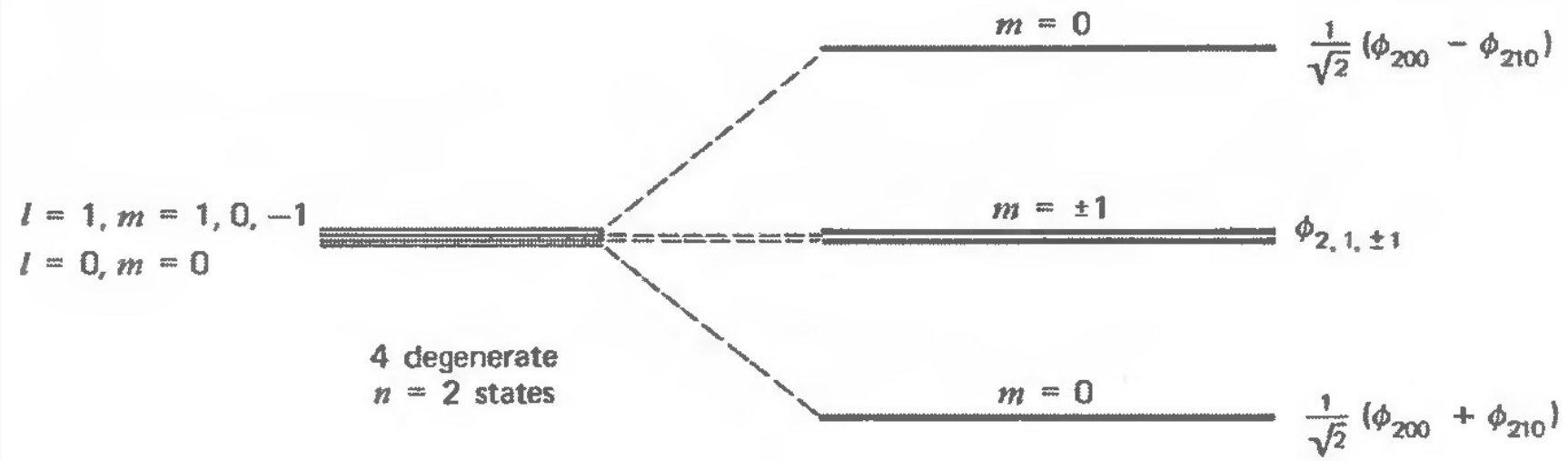
and the corresponding eigenstates, when properly normalized are, ewspectively

$$\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} \quad \text{and} \quad \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

Thus the linear stark effect for the n=2 states yields a splitting of degenerate levels as shown below:



$$\left|\Psi_n\right\rangle = N(\lambda)\left\{\sum_i \alpha_i \left|\Phi_n^{(i)}\right\rangle + \lambda \sum_{k\neq n} C_{nk}^{(1)} \sum_i \beta_i \left|\Phi_k^{(i)}\right\rangle + \ldots\right\}$$



$$\left|\Psi_n\right\rangle = N(\lambda)\sum_i \alpha_i \left|\Phi_n^{(i)}\right\rangle$$

$$\frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix} \quad \text{and} \quad \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix}$$

$$N(\lambda)\begin{pmatrix}\alpha_1\\\alpha_2\end{pmatrix}$$

There are some general comments that can be abstracted from the calculations just concluded:

(a) The states in the presence of the electric field are no longer eigenstates of L^2, since:

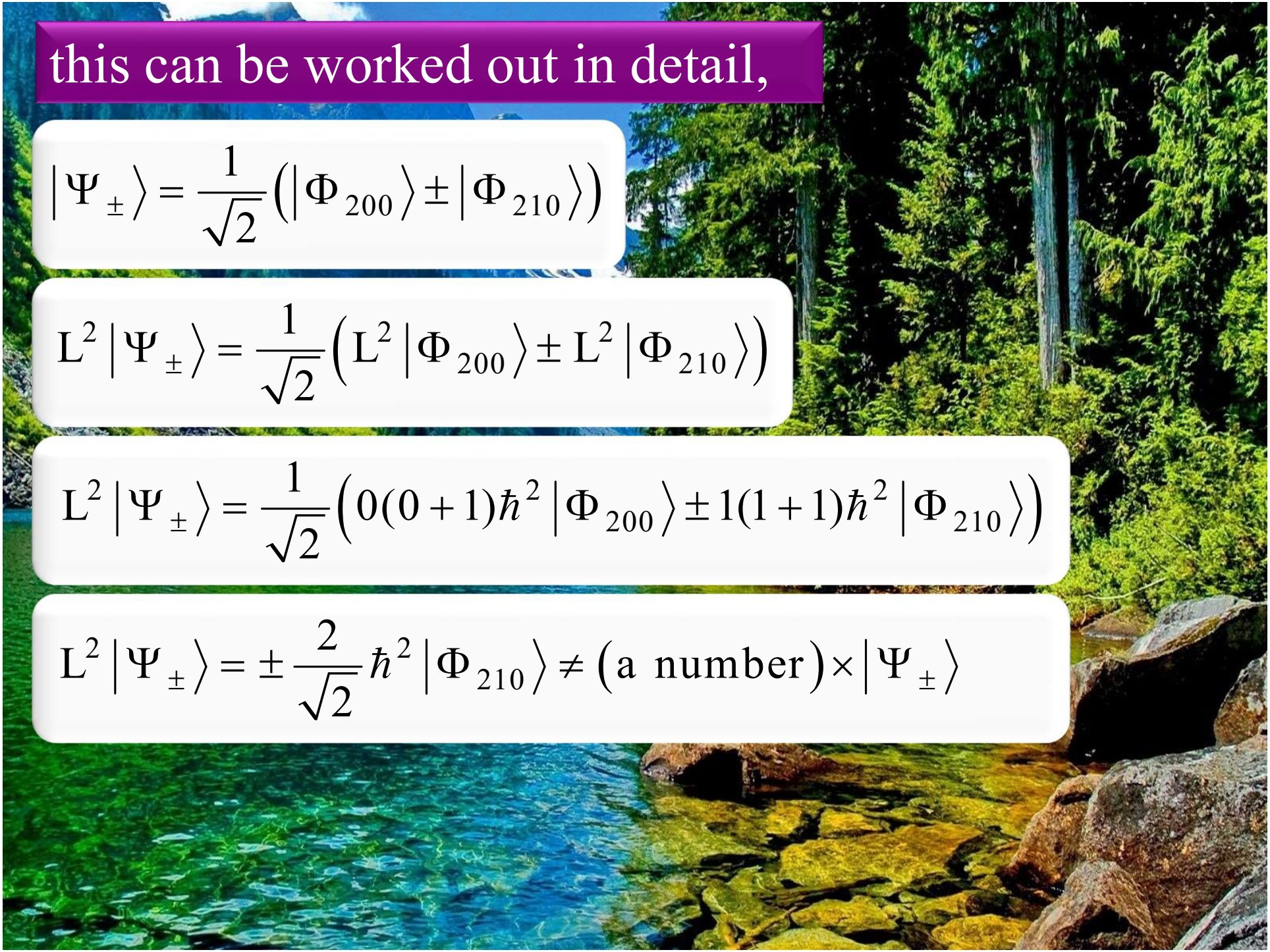
the states that diagonalize the perturbation were equal mixtures of $l=0$ and $l=1$, though they are still eigenstates of L_z,

this can be worked out in detail,

but it is really evident,

because the external field specifies a preferred direction, so that

the physical system is no longer invariant under arbitrary rotations.



this can be worked out in detail,

$$|\Psi_{\pm}\rangle = \frac{1}{\sqrt{2}}\left(|\Phi_{200}\rangle \pm |\Phi_{210}\rangle\right)$$

$$L^2|\Psi_{\pm}\rangle = \frac{1}{\sqrt{2}}\left(L^2|\Phi_{200}\rangle \pm L^2|\Phi_{210}\rangle\right)$$

$$L^2|\Psi_{\pm}\rangle = \frac{1}{\sqrt{2}}\left(0(0+1)\hbar^2|\Phi_{200}\rangle \pm 1(1+1)\hbar^2|\Phi_{210}\rangle\right)$$

$$L^2|\Psi_{\pm}\rangle = \pm\frac{2}{\sqrt{2}}\hbar^2|\Phi_{210}\rangle \neq (\text{a number})\times|\Psi_{\pm}\rangle$$

(b) Quite generally, whenever there is a perturbation that does not conserve some quantity (for example, L^2 here),

$$[H, L^2] \neq 0$$

$$[H, L^2] = -i\hbar \frac{dL^2}{dt}$$

$$\frac{dL^2}{dt} \neq 0$$

perturbation does not conserve L^2.

then the states that diagonalize the new Hamiltonian in any approximation, are superposition of states with different values of the previously conserved quantum numbers, and degenerate levels will be split.

(c) We may summarize the procedure in degenerate perturbation theory in matrix language as follows.

If H_0 is diagonal, but H, is not, then since H_0 and H_1 do not commute, it is not possible to diagonalize H_1 by itself, without "un-diagonalizing" H_0.

One must work with $H = H_0 + H_1$ as a whole.

If we work with a subset of degenerate states, all of which are eigenstates of H_0 with the same eigenvalue, then as far as these states are concerened, H_0 is not merely diagonal, but it is proportional to the unit matrix.

Since H_1 (and everything else) commute with the unit matrix, one may diagonalize H_1 by itself, without affecting H_0.

The hydrogenlike atoms considered here were somewhat idealize.

As we see in chapter 17, there are small relativistic and spin-orbit coupling effects that actually remove some of the degeneracies.

Does this mean that we never need to use degenerate perturbation theory?

Actually, even if, say, ϕ_{200} and ϕ_{210} do not have exactly the same energy, it may be still sensible to take some linear combination of them in the perturbation expansion.

If we have, for example

$$H_0\Phi_{200} = \left(E_2^0 - \Delta\right)\Phi_{200}$$

$$H_0\Phi_{210} = \left(E_2^0 + \Delta\right)\Phi_{210}$$

with Δ small, then the Schrodinger equation, with the linear combinations, reads

$$\left(H_0 + \lambda H_1\right)\left(\alpha_1\Phi_{200} + \alpha_2\Phi_{210} + \lambda\sum_{n\neq 2} C_n\Phi_n\right)$$

$$= E\left(\alpha_1\Phi_{200} + \alpha_2\Phi_{210} + \lambda\sum_{n\neq 2} C_n\Phi_n\right)$$

Taking the scalar product with ϕ_{200} and ϕ_{210}, respectively, leads to the following equation to order λ:

$$\begin{pmatrix} E_2^0 - \Delta - \langle \Phi_{200} | \lambda H_1 | \Phi_{200} \rangle & \langle \Phi_{200} | \lambda H_1 | \Phi_{210} \rangle \\ \langle \Phi_{210} | \lambda H_1 | \Phi_{200} \rangle & E_2^0 + \Delta - \langle \Phi_{210} | \lambda H_1 | \Phi_{210} \rangle \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} = E \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix}$$

If we write

$$\langle \Phi_{200} | \lambda H_1 | \Phi_{210} \rangle = \langle \Phi_{210} | \lambda H_1 | \Phi_{200} \rangle = a\lambda$$

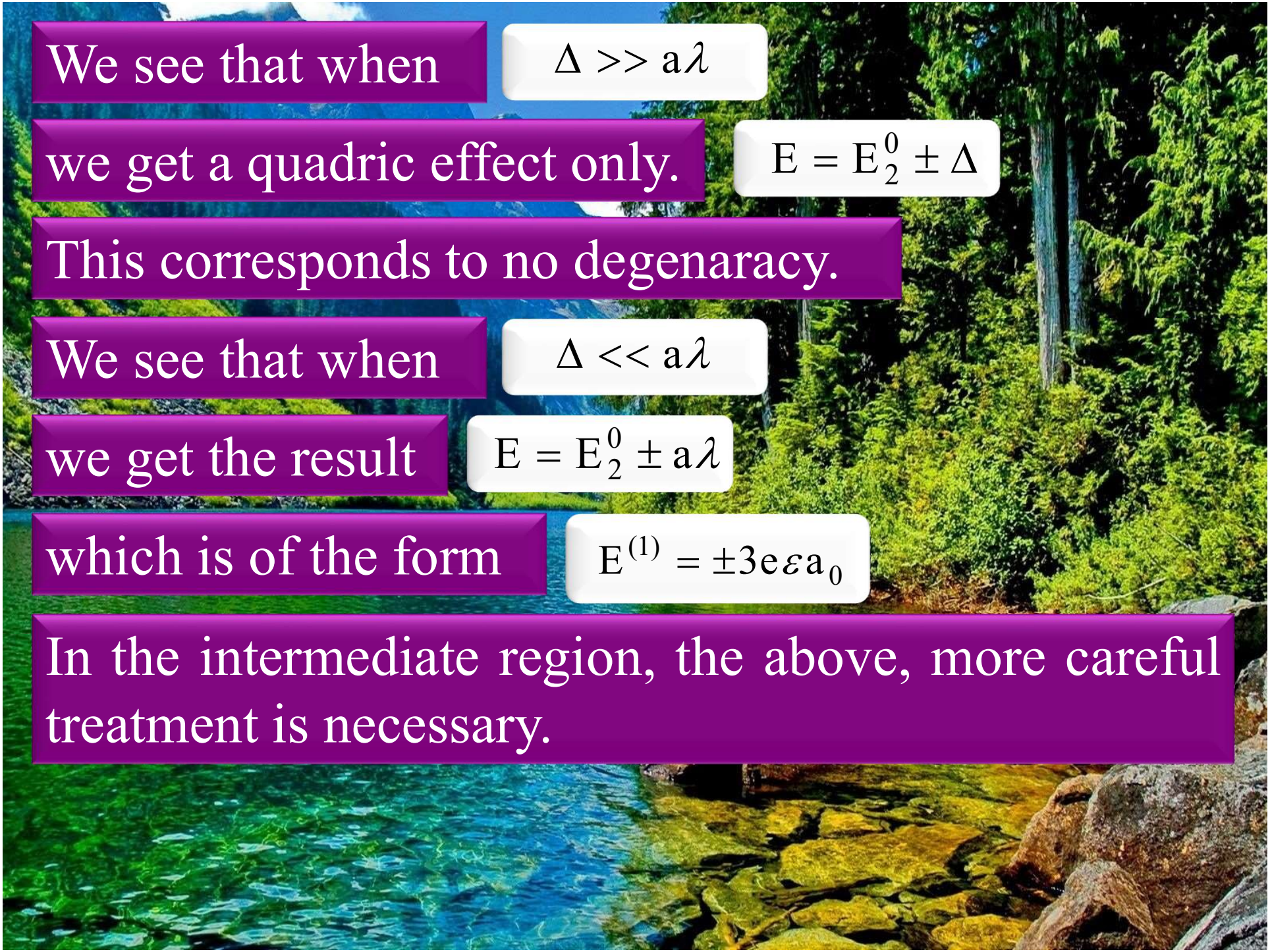
$$\langle \Phi_{200} | H_1 | \Phi_{200} \rangle = \langle \Phi_{210} | H_1 | \Phi_{210} \rangle = 0$$

we must find the eigenvalues of the matrix

$$\begin{pmatrix} E_2^0 - \Delta & \lambda a \\ \lambda a & E_2^0 + \Delta \end{pmatrix}$$

and these are

$$E = E_2^0 \pm \sqrt{a^2 \lambda^2 + \Delta^2}$$


We see that when
$\Delta >> a\lambda$
we get a quadric effect only.
$E = E_2^0 \pm \Delta$
This corresponds to no degenaracy.
We see that when
$\Delta << a\lambda$
we get the result
$E = E_2^0 \pm a\lambda$
which is of the form
$E^{(1)} = \pm 3e\varepsilon a_0$
In the intermediate region, the above, more careful treatment is necessary.

Furthermore, when the new linear combinations are used, then in second order perturbation theory there no longer appear very tiny energy differences in the denominators.

We do not discuss this in detail, but this is not difficult to establish.

As a final comment we point out two apparently contradictory facts.

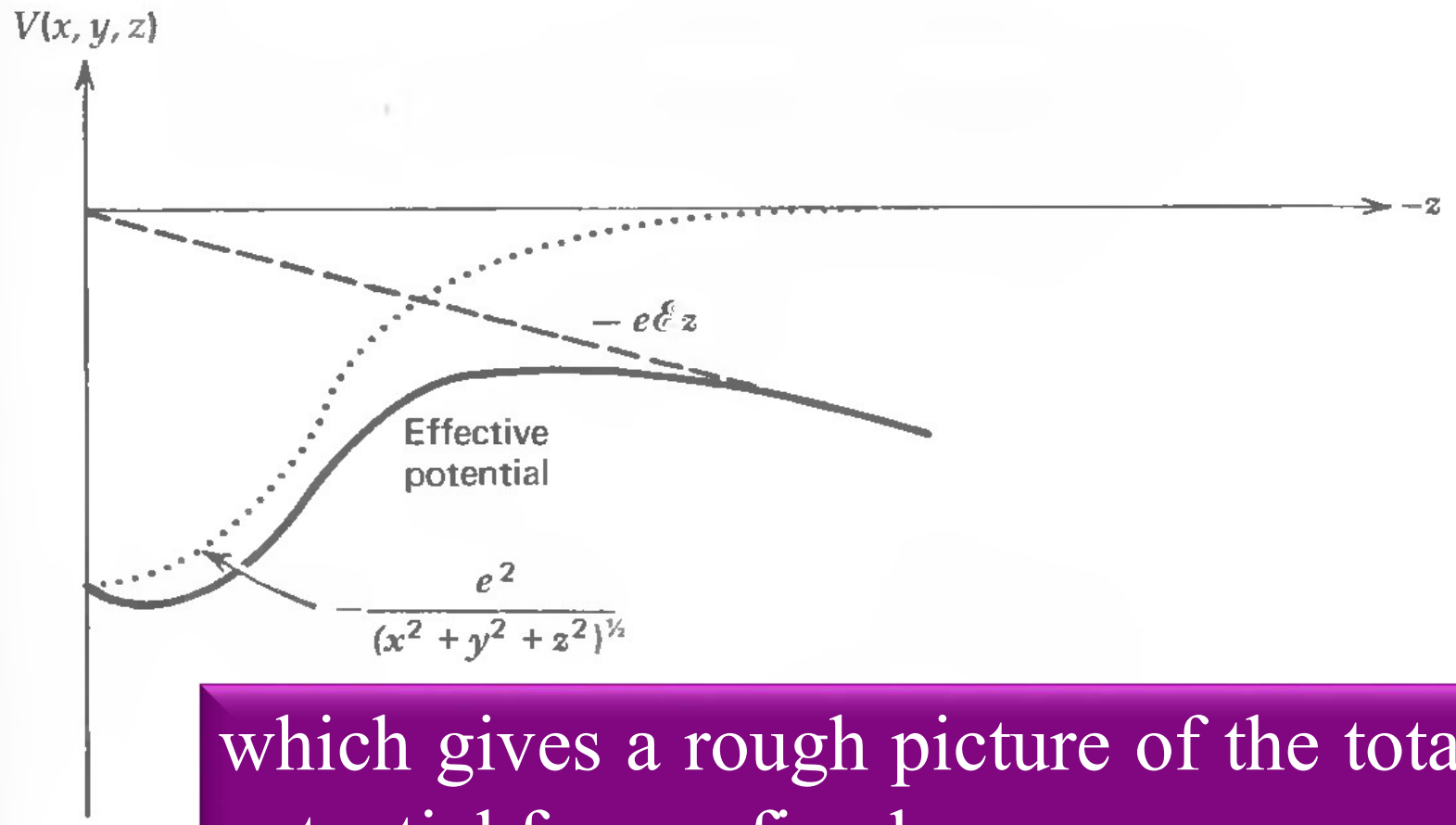
(1) The predictions of perturbation theory concerning the Stark effect are born out very well by experiment.

(2) The perturbation series evidently diverges, since the perturbing potential eεz grows without bound as z becomes very large, no matter how small eε is.

The question arises whether one has any right to believe in the accuracy of the first few terms of a mathematically divergent series, since it is well known that a mathematically divergent series can be rearranged to give entirely different expansions.

The answer lies in the physics and not in the mathematics of the problem.

The reason for the divergence can be seen in the following figure:

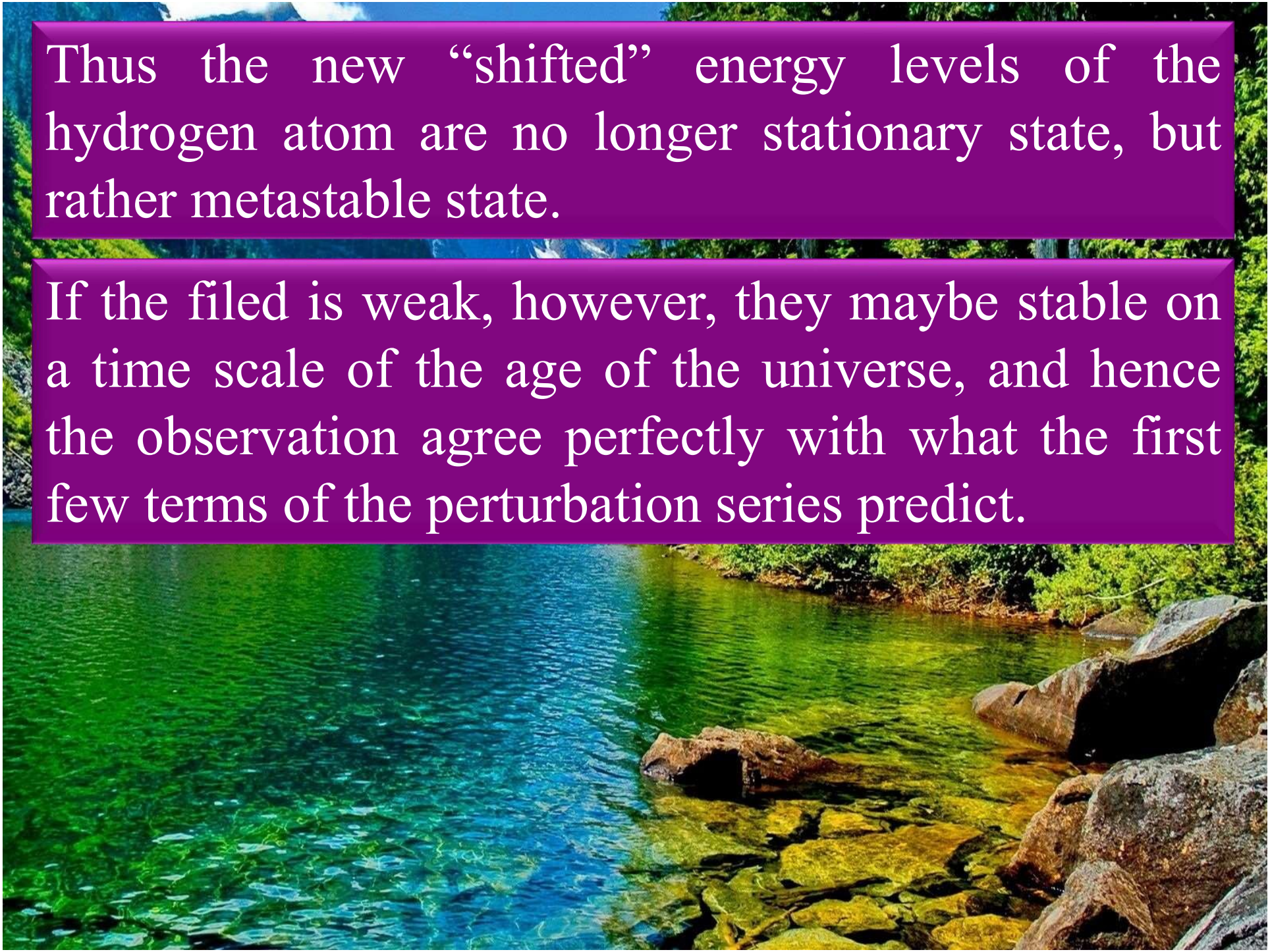


which gives a rough picture of the total potential for x,y fixed.

It appears that there is a barrier created for the bound electron.

This barrier is ultimately penetrable, even though for small $e\varepsilon$ it is very broad.

What the mathematical divergence of the series is responding to is the possibility that the electron in the ground state, for example, has a finite (although very, very small) probability of being sufficiently far away from nucleus, where the external electric field is stronger than the Coulomb field, and the electron is carried away by the electric filed.



Thus the new “shifted” energy levels of the hydrogen atom are no longer stationary state, but rather metastable state.

If the filed is weak, however, they maybe stable on a time scale of the age of the universe, and hence the observation agree perfectly with what the first few terms of the perturbation series predict.