Perturbation Theory

We begin our discussion of perturbation theory by returning to solve a 3-D problem: effect of a uniform magnetic field on the central force problem.

We need to find the operator form of the electromagnetic interaction. We know that in classical e-m theory

$$F = q\vec{E} + q\frac{\vec{v}\times\vec{B}}{c}.$$

(Jackson's notation $q\frac{\vec{v}}{c}\times\vec{B}$; Corson & Lorrain $q\vec{v}\times\vec{B}$).

The number of independent variables can be reduced through the introduction of the scalar and vector potential Φ & $\vec{A}$ (both functions of $\vec{r}$):

$$\vec{E}(r) = -\vec{\nabla}\Phi(r) \qquad \vec{B}(r) = \vec{\nabla}\times\vec{A}(r)$$

(↑ we have dropped the time dependence; otherwise $\vec{E} = -\nabla\Phi - \frac{\partial A}{\partial t}$)

The potential, expressed in terms of these quantities, is

$$U = q\Phi - \frac{q}{c}\vec{v}\cdot\vec{A} \qquad [U \text{ is velocity dependent}]$$

Proof: $\mathcal{L} = \frac{1}{2}m\dot{x}^2 - U(x,\dot{x})$ + Lagrange's Equations $\frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{x}}\right) = \frac{\partial \mathcal{L}}{\partial x}$

$$\frac{d}{dt}\left(\frac{\partial}{\partial \dot{x}}\left[\frac{1}{2}m\dot{x}^2 - U(x,\dot{x})\right]\right) = \frac{\partial}{\partial x}\left(\frac{1}{2}m\dot{x}^2 - U\right)$$

$$\Rightarrow \frac{d}{dt}(m\dot{x}) - \frac{d}{dt}\left(\frac{\partial U}{\partial \dot{x}}\right) = -\frac{\partial U}{\partial x} \qquad \text{But } F = m\ddot{x} \Rightarrow F = -\frac{\partial U}{\partial x} + \frac{d}{dt}\left(\frac{\partial U}{\partial \dot{x}}\right)$$

$$\Rightarrow \quad F_x = -q\frac{\partial}{\partial x}\Phi + \frac{q}{c}\frac{\partial}{\partial x}(\vec{v}\cdot\vec{A}) + \underbrace{\frac{d}{dt}\left(-\frac{q}{c}\frac{\partial}{\partial v_x}(\vec{v}\cdot\vec{A})\right)}$$

$$\hookrightarrow -\frac{q}{c}\cdot 1\cdot\frac{dA_x}{dt} = -\frac{q}{c}\left(\frac{\partial A_x}{\partial x}\frac{\partial x}{\partial t} + \frac{\partial A_x}{\partial y}\frac{\partial y}{\partial t} + \frac{\partial A_x}{\partial z}\frac{\partial z}{\partial t}\right)$$

$$= -\frac{q}{c}\left[\frac{\partial A_x}{\partial x}v_x + \frac{\partial A_x}{\partial y}v_y + \frac{\partial A_x}{\partial z}v_z\right]$$

$$= -\frac{q}{c}\vec{v}\cdot\vec{\nabla}A_x$$

$$\Rightarrow \quad F_x = -\frac{q}{c}\vec{v}\cdot(\vec{\nabla}A_x) - q\frac{\partial}{\partial x}\Phi + \frac{q}{c}\frac{\partial}{\partial x}(\vec{v}\cdot\vec{A})$$

$$\Rightarrow \quad \vec{F} = -\frac{q}{c}\vec{v}\cdot(\vec{\nabla}\vec{A}) - q\vec{\nabla}\Phi + \frac{q}{c}\vec{\nabla}(\vec{v}\cdot\vec{A}) \qquad \text{OK}$$

Lastly, use $\vec{\nabla}(\vec{v}\cdot\vec{A}) = \vec{v}\cdot\vec{\nabla}\vec{A} + \vec{v}\times(\vec{\nabla}\times\vec{A})$ ①

$$\Rightarrow \vec{F} = -q\vec{\nabla}\Phi + \frac{q}{c}\vec{v}\times(\vec{\nabla}\times\vec{A})$$

$$= -q\vec{E} + \frac{q}{c}\vec{v}\times\vec{B} \qquad \text{QED.}$$

So, the Lagrangian corresponding to this is:

$$\mathcal{L} = T - U = \frac{1}{2}mv^2 + \frac{q}{c}\vec{A}\cdot\vec{v} - q\Phi\,.$$

To find the Hamiltonian: $\mathcal{H} = \sum_{i=1}^{3} p_i\dot{q}_i - \mathcal{L}$

Use: $p_i = \frac{\partial\mathcal{L}}{\partial\dot{q}_i} = \frac{2}{2}m\dot{q}_i + \frac{q}{c}A_i \Rightarrow \dot{q}_i = \frac{p_i - qA_i/c}{m}$

$$\Rightarrow \mathcal{H} = \sum_{i=1}^{3} p_i\left(\frac{p_i - qA_i/c}{m}\right)^{①} - \frac{1}{2}m\sum_i\left(\frac{p_i - qA_i/c}{m}\right)^{2\,②} - \frac{q}{c}\sum_{i=1}^{3}A_i\left(\frac{p_i - \frac{q}{c}A_i}{m}\right)^{③} + q\Phi$$

$$\overset{①+③}{=} \frac{1}{m}\sum_{i=1}^{3}\left(p_i - \frac{q}{c}A_i\right)^2 - \frac{1}{2m}\sum_i\left(p_i - \frac{q}{c}A_i\right)^2 + q\Phi = \frac{1}{2m}\left(\vec{p} - \frac{q}{c}\vec{A}\right)^2 + q\Phi\,.$$

Effect of a Uniform magnetic field on the Central Force Problem

Suppose $\vec{B}$ is uniform, i.e. $\frac{\partial\vec{B}}{\partial x_i} = 0$.

Then the form for $\vec{A}$ can be seen to be $\vec{A} = \frac{1}{2}\vec{B}\times\vec{r}$. ②

This form for $\vec{A}$ satisfies:

$$\Rightarrow \vec{B} = \vec{\nabla}\times\vec{A} = \vec{\nabla}\times\left(\frac{1}{2}\vec{B}\times\vec{r}\right) = \frac{1}{2}\left[(\vec{\nabla}\cdot\vec{r})\vec{B} - (\vec{\nabla}\vec{r})\cdot\vec{B}\right] = \frac{1}{2}\left[3\vec{B} - \vec{B}\right] = \vec{B}\,.$$

This is $\left(\frac{d}{dx}x\right)\cdot B_x + \frac{d}{dy}y\,B_y$ etc

Then the Hamiltonian must be of the form: ($V(r)$ is the central force)

$$\mathcal{H} = \frac{p^2}{2m} + V(r) - \frac{q}{mc}\vec{p}\cdot\vec{A} + \frac{q^2}{2mc^2}\vec{A}^2 \qquad (\Phi = 0)$$

$$= \frac{p^2}{2m} + V(r) - \frac{q}{2mc}\vec{p}\cdot(\vec{B}\times\vec{r}) + \frac{q^2}{2mc^2}\left|\frac{1}{2}\vec{B}\times\vec{r}\right|^2$$

rearrange — neglect for weak fields.

$$\vec{p}\cdot(\vec{B}\times\vec{r}) = (\vec{r}\times\vec{p})\cdot\vec{B} \qquad (3)$$

Then defines $\frac{q}{2mc}\vec{r}\times\vec{p} = \frac{q}{2mc}\vec{L} \equiv \vec{\mu}$ (orbital magnetic dipole moment).

Now, choosing $\vec{B}$ to lie along the z-axis gives

$\vec{B}\cdot\vec{L} = B\hat{L}_z$ in operator form.

$$\Rightarrow \hat{\mathcal{H}} = \frac{\hat{p}^2}{2m} - \frac{q}{2mc}B\hat{L}_z + V(r).$$

Defining these as the "original" central Hamiltonian, $\equiv \hat{\mathcal{H}}_{cf}$

we see that

$$[\hat{\mathcal{H}}, \mathcal{H}_{cf}] = 0 \quad \text{since} \quad [\hat{\mathcal{H}}_{cf}, \hat{L}_z] = 0.$$

This means that $\hat{\mathcal{H}}$ and $\hat{\mathcal{H}}_{cf}$ have a common set of eigenfunctions ψ_{nlm_l}.

$$\Rightarrow \hat{\mathcal{H}}\psi_{nlm} = \mathcal{H}_{cf}\psi_{nlm_l} - \frac{q}{2mc}B\hat{L}_z\psi_{nlm_l}$$

$$= \left(\epsilon_{nlm} - \frac{q}{2mc}(m_l\hbar)B\right]\psi_{nlm_l} \Leftarrow \begin{pmatrix}q \text{ still has a} \\ \text{sign, +e or −e}\end{pmatrix}$$

Here, μ_B is defined as the Bohr magneton, whose value depends on the mass and charge of the particle in question:

$$\mu_B = \frac{e\hbar}{2mc}$$

What has happened to the energy levels is that they have been "split" apart by the applied magnetic field. This is known as the "normal" Zeeman effect ("Anomolous" Zeeman effect includes spin). Note that the splitting depends only on m_ℓ

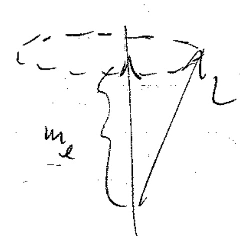
$$\epsilon = \epsilon_{n\ell m} - \frac{(-e)}{2mc} m_\ell \hbar B$$
$$= \epsilon_{n\ell m} + \frac{e m_\ell \hbar B}{2mc}$$

	no B		B
1s	$(n=1, \ell=0)$	$\longrightarrow$	$n=1, \ell=0, m_\ell=0$
			$(n=2, \ell=1, m_\ell=+1)$
degenerate { 2s, 2p	$n=2, \ell=1$; $n=2, \ell=0$		$(n=2, \ell=0, m_\ell=0)$, $(n=2, \ell=1, m_\ell=0)$ } degenerate
			$(n=2, \ell=1, m_\ell=-1)$

Classically, what's happening is that the $\vec{L}$ vector is precessing about $\vec{B}$, with a precession angular frequency given by

$$\underline{\omega}\,\hbar = \frac{e\hbar}{2mc}B \Rightarrow \omega = \frac{eB}{2mc}.$$

Larmor frequency



Perturbation Theory

In the previous example, we made use of an approximate Hamiltonian in the weak field limit (i.e., we set the B^2 term $= 0$). This approximate Hamiltonian commuted with the original one, allowing the eigenvalues to be found almost trivially. We now wish to generalize this result (although the general case is not strictly parallel to the Zeeman effect) with the idea that we express a problem as:

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_o + \lambda \hat{V}$$

$\hat{\mathcal{H}}_o$: some Hamiltonian for which we know the solution

$\lambda \hat{V}$ is a "perturbing potential", λ being a small number.

Now, there is a heirarchy of difficulty in attacking this problem:

Hard

③ Time dependent V, degenerate states

② Time independent V, degenerate states

① Time independent V, non-degenerate states.

We begin with ①.

Non-Degenerate Bound State
Stationary perturbation Theory [Rayleigh - Schroedinger method]
originally applied to sound.

We have an "unperturbed" Hamiltonian characterized by:

$$\hat{\mathcal{H}}_0 | \epsilon_i^0 \rangle = \epsilon_i^0 | \epsilon_i^0 \rangle$$

Perturbed Hamiltonian:

$$\hat{\mathcal{H}} | \epsilon_i \rangle = (\hat{\mathcal{H}}_0 + \lambda \hat{V}) | \epsilon_i \rangle = \epsilon_i | \epsilon_i^0 \rangle$$

Now, we assume that $| \epsilon_i \rangle \xrightarrow[\lambda \to 0]{} | \epsilon_i^0 \rangle$ (The obvious problem with ... - degenerate states is that they are not unique and hence the smoothness relation $\lambda \to 0$ may be difficult to implement).
We define a set of eigenvectors with the perturbed Hamiltonian by:

$$\epsilon_i = \epsilon_0 + \lambda \epsilon_i^{(1)} + \lambda^2 \epsilon_i^{(2)} \ldots$$

$$| \epsilon_i \rangle = | \epsilon_i^0 \rangle + \lambda | \epsilon_i^{(1)} \rangle + \lambda^2 | \epsilon_i^{(2)} \rangle$$

$\Rightarrow$ $\hat{\mathcal{H}} | \epsilon_i \rangle = \epsilon_i | \epsilon_i \rangle$ becomes

$$(\hat{\mathcal{H}}_0 + \lambda \hat{V}) \{ | \epsilon_i^0 \rangle + \lambda | \epsilon_i^{(1)} \rangle + \lambda^2 | \epsilon_i^{(2)} \rangle \cdots \}$$

$$= \{ \epsilon_i^0 + \lambda \epsilon_i^{(1)} + \lambda^2 \epsilon_i^{(2)} \cdots \} \{ | \epsilon_i^0 \rangle + \lambda | \epsilon_i^{(1)} \rangle + \lambda^2 | \epsilon_i^{(2)} \rangle \cdots \}$$

Collecting terms in λ:

$$\Rightarrow \left[\hat{\mathcal{H}}_0|\epsilon_i^{0}\rangle - \epsilon_i^{0}|\epsilon_i\rangle\right] + \lambda\left[\hat{\mathcal{H}}_0|\epsilon_i^{(1)}\rangle + \hat{V}|\epsilon_i^{(0)}\rangle - \epsilon_i^{0}|\epsilon_i^{(1)}\rangle - \epsilon_i^{(1)}|\epsilon_i^{(0)}\rangle\right]$$

$$+\lambda^2\left[\hat{\mathcal{H}}_0|\epsilon_i^{(2)}\rangle + \hat{V}|\epsilon_i^{(1)}\rangle - \epsilon_i^{(1)}|\epsilon_i^{(1)}\rangle - \epsilon_i^{0}|\epsilon_i^{(2)}\rangle - \epsilon_i^{(2)}|\epsilon_i^{0}\rangle\right] + \cdots$$

$$= 0.$$

Since this should be valid for all λ, each coefficient should vanish separately:

$$\hat{\mathcal{H}}_0|\epsilon_i^{0}\rangle = \epsilon_i^{(0)}|\epsilon_i^{(0)}\rangle \quad \leftarrow \text{just a restatement.}$$

$$\hat{\mathcal{H}}_0|\epsilon_i^{(1)}\rangle + \hat{V}|\epsilon_i^{(0)}\rangle = \epsilon_i^{(0)}|\epsilon_i^{(1)}\rangle + \epsilon_i^{(1)}|\epsilon_i^{(0)}\rangle \quad \leftarrow 1^{\text{st}} \text{ order}$$

$$\hat{\mathcal{H}}_0|\epsilon_i^{(2)}\rangle + \hat{V}|\epsilon_i^{(1)}\rangle = \epsilon_i^{(1)}|\epsilon_i^{(1)}\rangle + \epsilon_i^{(0)}|\epsilon_i^{(2)}\rangle + \epsilon_i^{(2)}|\epsilon_i^{(0)}\rangle \quad \leftarrow 2^{\text{nd}} \text{ order.}$$

Let's take the 1^{st} order theory & solve for $|\epsilon_i^{(1)}\rangle$. Since $|\epsilon_i^{(0)}\rangle$ are a complete set of orthonormal states, then we can expand.

$$|\epsilon_i^{(1)}\rangle = \sum_{j=1} a_{ij}^{(1)}|\epsilon_j^{(0)}\rangle$$

To solve for the a_{ij}, we substitute into the first order equ.

$$\hat{\mathcal{H}}_0\sum_j a_{ij}^{(1)}|\epsilon_j^{(0)}\rangle + \hat{V}|\epsilon_i^{(0)}\rangle = \epsilon_i^{(0)}\sum_j a_{ij}^{(1)}|\epsilon_j^{(0)}\rangle + \epsilon_i^{(1)}|\epsilon_i^{(0)}\rangle$$

$$\Rightarrow \sum_j(\epsilon_j^{0} - \epsilon_i^{0})a_{ij}|\epsilon_j^{(0)}\rangle = (\epsilon_i^{(1)} - \hat{V})|\epsilon_i^{(0)}\rangle$$

Close this equation with $\langle\epsilon_k^{(0)}|$ and use orthonormal condition

$$\sum_i(\epsilon_j^{0} - \epsilon_i^{0})a_{ij}\delta_{jk} = \epsilon_i^{(1)}\delta_{ik} - \langle\epsilon_k^{0}|\hat{V}|\epsilon_i^{0}\rangle$$

Let $k = i$

$$0 = \epsilon_i^{(1)} - V_{ii} \qquad \left(V_{ii} \equiv \langle i|\hat{V}|i\rangle\right)$$

or $\epsilon_i^{(1)} = V_{ii}$.

In other words, we now have $\epsilon_i = \epsilon_i^{\circ} + \lambda V_{ii}$

Continuing, $k \neq i$ and performing the j sum gives

$$(\epsilon_k^{\circ} - \epsilon_i^{\circ})a_{ik}^{(1)} = -\langle \epsilon_k^{\circ}|\hat{V}|\epsilon_i^{\circ}\rangle$$

$$\text{or} \quad a_{ik}^{(1)} = \frac{V_{ki}}{\epsilon_i^{\circ} - \epsilon_k^{\circ}}$$

This tells us a_{ik}, but not a_{ii}.

So long as we have no degeneracy, this operation is ok.

$$\Rightarrow \quad |\epsilon_i\rangle = |\epsilon_i^{(0)}\rangle + \lambda a_{ii}^{(1)}|\epsilon_i^{(0)}\rangle + \lambda \sum_{j \neq i} \frac{V_{ji}}{\epsilon_i^{(0)} - \epsilon_j^{(0)}}|\epsilon_j^{(0)}\rangle$$

still to be determined from normalization of $|\epsilon_i\rangle$.

That is $|\epsilon_i^{(0)}\rangle + \lambda a_{ii}^{(1)}|\epsilon_i^{\circ}\rangle = (1 + \lambda a_{ii}^{(1)})|\epsilon_i^{\circ}\rangle$.

To do the normalization, close with $\langle \epsilon_i|$:

$$1 = \left\{(1 + \lambda a_{ii}^{(1)*})\langle\epsilon_i^{(0)}| + \lambda \sum_{j \neq i} \frac{V_{ji}^*}{\epsilon_i^{(0)} - \epsilon_j^{(0)}}\langle\epsilon_j^{(0)}|\right\}$$

$$\left\{(1 + \lambda a_{ii}^{(1)})|\epsilon_i^{(0)}\rangle + \lambda \sum \frac{V_{ji}}{\epsilon_i^{\circ} - \epsilon_j^{\circ}}|\epsilon_j^{\circ}\rangle\right\}$$

$$= |1 + \lambda a_{ii}^{(1)}|^2 \quad \left(\sum_j = 0 \text{ from orthonorm}\right) + O(\lambda^2)$$

$$= 1 + \lambda\left(a_{ii}^{(1)*} + a_{ii}^{(1)}\right) + O(\lambda^2)$$

$$\simeq 1 + 2\lambda \,\mathrm{Re}\, a_{ii}$$

or $\mathrm{Re}\, a_{ii} = 0$. Further, to first order in λ $\mathrm{Im}\, a_{ii}$ doesn't

Of course, all of these results go over into the coordinate representation:

$$E_i = E_i^{(0)} + \lambda V_{ii}$$

$$\psi_i = \psi_i^{\circ} + \lambda \sum_{j \neq i} \frac{V_{ji}}{E_i^{\circ} - E_j^{\circ}} \psi_j^{\circ}$$

$$V_{ji} = \int \psi_j^{\circ *} \hat{V}(-i\hbar\vec{\nabla}, \vec{r}) \psi_i \, d^3r .$$

(There are a corresponding set of equations for 2nd order which we will not cover)

Example

Anharmonic oscillator in 1-dimension:

$$\hat{\mathcal{H}} = \underbrace{\frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 x^2}_{\hat{\mathcal{H}}_0} + \underbrace{\lambda x^4}_{\text{anharmonic term.}}$$

$$\psi_n^{\circ} = \left[\left(\frac{\alpha}{\pi}\right)^{1/2} \left(\frac{1}{2^n n!}\right)\right]^{1/2} e^{-\alpha x^2/2} H_n(\sqrt{\alpha}\, x) \quad \text{with } \alpha = \frac{m\omega}{\hbar}.$$

$$E_n^{\circ} = (n + 1/2)\omega\hbar .$$

To find the energy shift, we evaluate:

$$\int \psi_n^{\circ *} \lambda x^4 \psi_n \, dx = \lambda \left[\left(\frac{\alpha}{\pi}\right)^{1/2} \frac{1}{(2^n n!)}\right] \int e^{-\alpha x^2} H_n^2(\sqrt{\alpha}\, x) x^4 \, dx .$$

Say we take the ground state energy $(n=0)$

$[\xi = \sqrt{\alpha}\, x]$

$$V_{00} = \lambda \left[\left(\frac{\alpha}{\pi}\right)^{1/2} \frac{1}{1}\right] \int e^{-\alpha x^2} H_0^2(\sqrt{\alpha}\, x) x^4 \, dx$$

Degenerate States

The difficult in dealing with the degenerate system is that some correspondence has to be made between the "shifted" energy levels after the application of the perturbation, and the degenerate set of initial states.

$$|\epsilon_i\rangle \xrightarrow[\lambda\to 0]{} \underline{|\tilde{\epsilon}_i^{\,o}\rangle}$$

specific choice of states among all of the possibilities. Refer to as "select set".

So, the question is, how do we determine the select set? We write the set as

$$|\tilde{\epsilon}_i^{\,o}\rangle = \sum_{j=1}^{S} b_{ij}\,|\epsilon_i^{\,o}\rangle$$

sum over only those s wavefunctions which are degenerate.

The coefficients b_{ij} are subject to the usual orthonormality condition

$$\langle\tilde{\epsilon}_i^{\,o}|\tilde{\epsilon}_j^{\,o}\rangle = \delta_{ij} = \sum_{j=1}^{S} |b_{ij}|^2$$

Once the select set has been formally introduced, we use it in the first order perturbation equation. Dealing with the i^{th} eigenvalue corresponding to an eigenfunction from the select set:

$$\hat{H}_o|\epsilon_i^{(1)}\rangle + \hat{V}\,|\tilde{\epsilon}_i^{\,o}\rangle = \epsilon_i^{\,o}\,|\epsilon_i^{(1)}\rangle + \epsilon_i^{(1)}\,|\tilde{\epsilon}_i^{\,o}\rangle$$

Replace $|\epsilon_i^{(1)}\rangle$ as before with

$$|\epsilon_i^{(1)}\rangle = \sum_{j=1}^{\infty} a_{ij}^{(1)}\,|\epsilon_j^{(0)}\rangle \qquad \Big\|\ \text{order these } 1\ldots s,\ s+1\ldots\infty$$

So that

$$\sum_{j=1}^{\infty} a_{ij}^{(1)} \epsilon_j^\circ |\epsilon_j^\circ\rangle + \sum_{j=1}^{s} \hat{V} b_{ij} |\epsilon_j^\circ\rangle = \epsilon_i^\circ \sum_{j=1}^{\infty} a_{ij}^{(1)} |\epsilon_j^{(0)}\rangle + \epsilon_i^{(1)} \sum_{j=1}^{s} b_{ij} |\epsilon_j^\circ\rangle$$

For the first s states (remember they are ordered), $\epsilon_j^\circ = \epsilon_i^\circ = \epsilon^\circ$ and the 1^{st} s-terms in the infinite sums on the left and right hand sides cancel:

$$\sum_{j=1}^{s} a_{ij}^{(1)} \epsilon_j^\circ |\epsilon_j^\circ\rangle = \epsilon_i^{(0)} \sum_{j=1}^{s} a_{ij}^{(1)} |\epsilon_j^{(0)}\rangle = \epsilon_i^\circ \sum a | \rangle \,.$$

$\Rightarrow$ Equation to be solved is

$$\sum_{j>s}^{\infty} a_{ij}^{(1)} \epsilon_j^\circ |\epsilon_j^\circ\rangle + \sum_{j=1}^{s} \hat{V} b_{ij} |\epsilon_j^\circ\rangle = \epsilon_i \sum_{j>s}^{\infty} a_{ij}^{(1)} |\epsilon_j^\circ\rangle + \epsilon_i^{(1)} \sum_{j=1}^{s} b_{ij} |\epsilon_j^\circ\rangle$$

Next, close with $\langle\epsilon_k^\circ|$ with $k=1,\cdots s$ range:

$$0 + \sum_{j=1}^{s} b_{ij} \langle\epsilon_k^\circ|\hat{V}|\epsilon_j^\circ\rangle = 0 + \epsilon_i^{(1)} \sum_{j=1}^{s} b_{ij}\,\delta_{kj}$$

$$\text{or} \quad \sum_{j=1}^{s} V_{kj} b_{ij} = \epsilon_i^{(1)} b_{ik}.$$

This looks like an eigenvalue problem:

$$\vec{V}\vec{b}_i = \epsilon_i^{(1)} \vec{b}_i$$

ie.

$$\begin{pmatrix} V_{11} & \cdots & V_{1s} \\ V_{s1} & & V_{ss} \end{pmatrix} \begin{pmatrix} b_{i1} \\ \vdots \\ b_{is} \end{pmatrix} = \epsilon_i^{(1)} \begin{pmatrix} b_{i1} \\ \vdots \\ b_{is} \end{pmatrix} \qquad i=1,\cdots s.$$

(subject to normalization restriction).

Solving this equation (knowing V_{ij}) leads to

i) the determination of the b's ...
ii) the determination of the $\epsilon_i^{(1)}$'s, which is what we are after. Then we simply use
$$\epsilon_i = \epsilon_i^0 + \lambda \epsilon_i^{(1)}$$ so determined.

Lastly, had we started with the select case right at the beginning, we could have proceeded with the non-degenerate theory as before.

Example: Application of an electric field to Hydrogen (Stark effect).

The Stark effect involves the application of a uniform electric field along an axis. This results in an extra term in the Hamiltonian:

$$\int e\vec{E}\, d\vec{r} = e\vec{E}\cdot\vec{r}.$$

$E \uparrow\uparrow\uparrow\uparrow$

↑ +ve charge wants to move in +ve z-direction. It takes energy to move -ve charge in +ve direction.

$$\Rightarrow \hat{\mathcal{H}} = \frac{\hat{p}^2}{2m} - \frac{e^2}{r} + e\vec{E}\cdot\vec{r}.$$

Choose $\vec{E}$ to be along the z axis and write this as $\underbrace{eE}_{\lambda} \cdot \underbrace{z}_{\hat{V}}$

For the hydrogen ground state:

$$\lambda \epsilon^{(1)} = eE \int \underbrace{\psi_{1s}^{*}\, z\, \psi_{1s}}_{\text{isotropic.}}\, dz = 0$$

So no first order shift.

For the 2s,2p states, we have a fourfold degeneracy

n	l	m
2	0	0
2	1	-1
2	1	0
2	1	-1

$\rightarrow$ 4 states $\Rightarrow$ 4×4 V_{ij} matrix $\begin{pmatrix} V_{00} & & \\ & \ddots & \\ & & V_{1\text{-}1} \end{pmatrix}$

[All diagonal elements vanish by parity. only non-vanishing off-diagonal elements have $m=0$.]

Now, $z = r\cos\theta \;\propto\; Y_{10}$. This symmetry leads to the vanishing of V_{ij} between states with different m_l. (ie $\langle 211|z|210\rangle = 0$ etc). Further, the integrals

$\langle 21{\pm1}|z|21{\pm1}\rangle$ vanish as well. [Parity argument again].

Indeed $\langle 200|z|200\rangle = 0$
$\langle 210|z|210\rangle = 0$

So the $|21\pm1\rangle$ states decouple from the problem completely and they do not undergo a Stark shift. We are left with a 2×2 problem:

$$V_{ll'} = \begin{pmatrix} V_{00} & V_{10} \\ V_{01} & V_{11} \end{pmatrix}$$

But the diagonal components vanish.

Off diagonal components:

$$V_{10} = \int \psi^*_{210}\, r\cos\theta\, \psi_{200}\, r^2 dr\, d\cos\theta\, d\phi$$

$$= \int \frac{1}{4}\left(\frac{1}{2\pi a^3}\right)^{1/2}\left(\frac{r}{a}\right)e^{-r/2a}\cos\theta\cdot(r\cos\theta)\cdot\frac{1}{4}\left(\frac{1}{2\pi a^3}\right)^{1/2}\left(2-\frac{r}{a}\right) e^{-r/2a}\, r^2 dr\, d\cos\theta\, d\phi$$

[ψ from Weider, page 150]

$$= \frac{1}{16}\left(\frac{1}{2\pi a^3}\right)\int_0^{2\pi} d\varphi \int_{-1}^{1} \cos^2\theta \, d\cos\theta \int_0^{\infty} \left(\frac{r}{a}\right) r \left(2-\frac{r}{a}\right) e^{-r/a} r^2 dr$$

$$= \underbrace{\frac{1}{16a^3}\left(\frac{1}{3}x^3\Big|_{-1}^{1}\right) a^4}_{\frac{a}{24}} \underbrace{\int_0^{\infty} \xi^4 (2-\xi) e^{-\xi} d\xi}_{2\int_0^\infty \xi^4 e^{-\xi} d\xi \; - \; \int_0^\infty \xi^5 e^{-\xi} d\xi} .$$

Now $\displaystyle\int_0^{\infty} \xi^m e^{-\xi} d\xi = \Gamma(m+1) = m!$ $\leftarrow \left[\begin{array}{l} \frac{\partial}{\partial\alpha}\int_0^\infty e^{-\alpha\xi} \xi^{m-1} d\xi = -\int \xi \xi^{m-1} e^{-\alpha\xi} d\xi \\ \text{or } \int_0^\infty \xi^m e^{-\alpha\xi} d\xi = -\frac{\partial}{\partial\alpha}\int e^{-\alpha\xi} \xi^{m-1} d\xi \end{array}\right]$

$$\Rightarrow \text{Integral} = \frac{a}{24}\left[2 \cdot 4! - 5!\right]$$

$$= \frac{a}{24}\left[2 \times 24 - 5 \times 24\right] = -3a .$$

$\Rightarrow$ Eigenvalue equation is

$$\begin{vmatrix} 0-\epsilon & -3a \\ -3a & 0-\epsilon \end{vmatrix} = 0 \quad \Rightarrow \quad \epsilon^2 - (3a)^2 = 0$$

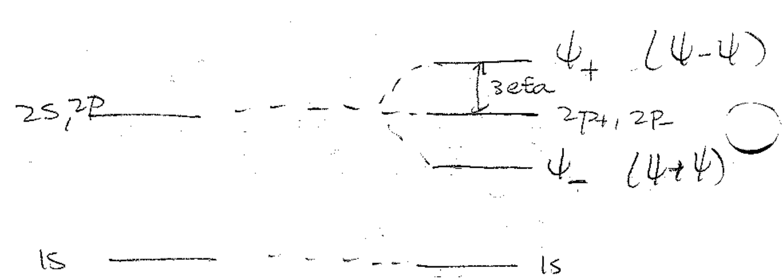
$$\epsilon = \pm 3a .$$

The corresponding eigenvectors are

$\epsilon = 3a$: $\left.\begin{array}{l} -3a c_1 \; - 3a c_2 = 0 \\ -3a c_1 \; - 3a c_2 = 0 \end{array}\right\} c_1 = -c_2$

$\epsilon = -3a$ $\qquad c_1 = +c_2$.

$\psi_+ \left(\overset{\text{i.e.}}{3a}\right) = \frac{1}{\sqrt{2}}(\psi_{200} - \psi_{210})$ $\qquad \psi_- \left(\overset{\text{i.e.}}{-3a}\right) = \frac{1}{\sqrt{2}}(\psi_{200} + \psi_{210})$



Supplementary material on vector products:

z-component, for example.

$$\vec{a}\times(\vec{b}\times\vec{c}) \Rightarrow a_x(b\times c)_y - a_y(b\times c)_x$$
$$= a_x(b_z c_x - b_x c_z) - a_y(b_y c_z - b_z c_y)$$
$$= c_z(-a_x b_x - a_y b_y) + b_z(a_x c_x + a_y c_y)$$
$$= c_z(-a_x b_x - a_y b_y - a_z b_z) + b_z(a_x c_x + a_y c_y + a_z c_z)$$
$$= -c_z(a\cdot b) + b_z(a\cdot c)$$
$$\Rightarrow \vec{a}\times(\vec{b}\times\vec{c}) = \vec{b}(\vec{a}\cdot\vec{c}) - \vec{c}(\vec{a}\cdot\vec{b}) \quad \text{(no operators)}.$$
$$= \vec{b}(\vec{a}\cdot\vec{c}) - (\vec{b}\cdot\vec{a})\vec{c}$$

Example: $\vec{\nabla}\times\vec{\nabla}\times\vec{A} = \vec{\nabla}(\vec{\nabla}\cdot\vec{A}) - (\vec{\nabla}\cdot\vec{\nabla})\vec{A}$ ①

Evaluate z-component of $\vec{\nabla}\times\vec{B}\times\vec{r}$ ②

z-comp. $\frac{d}{dx}(b_z c_x - b_x c_z) - \frac{d}{dy}(b_y c_z - b_z c_y)$

$$= b_z\left(\frac{d}{dx}c_x\right) - c_z\frac{d}{dx}b_x - c_z\frac{d}{dy}b_y + b_z\frac{d}{dy}c_y$$ ②
$$= b_z\left(\frac{d}{dx}c_x + \frac{d}{dy}c_y\right) - c_z\left(\frac{d}{dx}b_x + \frac{d}{dy}b_y\right)$$
$$= b_z(\vec{\nabla}\cdot\vec{c}) \underbrace{- b_z\frac{d}{dz}c_z - c_z\left(\frac{d}{dx}b_x + \frac{d}{dy}b_y\right)}_{-\frac{d}{dz}(b_z c_z) + c_z\left(\frac{d}{dz}b_z\right)}.$$
$$= b_z(\vec{\nabla}\cdot\vec{c}) - \frac{d}{dz}(\vec{b}\cdot\vec{c}) + c_z(\vec{\nabla}\cdot\vec{b})$$
$$\vec{\nabla}\times\vec{B}\times\vec{r} = \vec{B}(\vec{\nabla}\cdot\vec{r}) - \vec{\nabla}(\vec{r}\cdot\vec{B}) + \vec{r}(\vec{\nabla}\cdot\vec{B})$$ ②

$\frac{\partial B}{\partial x_i} = 0 \;\forall i$ then $\left\{ \quad 3\vec{B} \qquad \vec{B} + 0 \qquad = 0 \right.$

$$\vec{a}\cdot(\vec{b}\times\vec{c}) = a_x(b_y c_z - b_z c_y) + a_y(b_z c_x - b_x c_z) + a_z(b_x c_y - b_y c_x)$$
$$= b_x(c_y a_z - c_z a_y) + b_y(c_z a_x - c_x a_z) + b_z(c_x a_y - c_y a_x)$$
$$= \vec{b}\cdot(\vec{c}\times\vec{a})$$ ③