CAS PY 452 — Quantum Physics II

Emmy Blumenthal
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Discussion Notes

Email: emmyb320@bu.edu

Degenerate perturbation theory: 2×2

Problem: Find the energies, stationary states, and degeneracies of a spin-$\frac{1}{2}$ particle quadratically coupled to a magnetic field:

$$\hat{H}_0 = h_z \hat{S}_z^2, \tag{1}$$

where $\hat{S}_z$ is the z-spin operator for spin-$\frac{1}{2}$ and $h_z > 0$ is a constant with units of dimension $[\text{energy}]^{-1} \times [\text{time}]^{-2}$. Next, perturb the Hamiltonian as $\hat{H}_0 \to \hat{H}_0 + \hat{H}'$ where,

$$\hat{H}' = \lambda \hat{S}_y, \tag{2}$$

where $\lambda > 0$ is a constant with units of dimension $[\text{time}]^{-1}$ and $\lambda \ll h_z \hbar$. Find the first-order and second-order perturbed energies and the first-order perturbed states. Finally, compute the expected value of $\hat{S}_x$ for each perturbed state.

Solution: In the basis $\{|\uparrow\rangle, |\downarrow\rangle\}$, the spin-$\frac{1}{2}$ operators are,

$$[\hat{S}_x]_{\{|\uparrow\rangle,|\downarrow\rangle\}} = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad [\hat{S}_y]_{\{|\uparrow\rangle,|\downarrow\rangle\}} = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \qquad [\hat{S}_z]_{\{|\uparrow\rangle,|\downarrow\rangle\}} = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{3}$$

$$[\hat{S}_z^2]_{\{|\uparrow\rangle,|\downarrow\rangle\}} = \frac{\hbar^2}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \tag{4}$$

In case this matrix notation is unclear: for example, this means $\hat{S}_x |\uparrow\rangle = \frac{\hbar}{2}|\downarrow\rangle$ and $\hat{S}_y(|\uparrow\rangle + |\downarrow\rangle) = \frac{\hbar}{2}(-i|\uparrow\rangle + i|\downarrow\rangle)$. To find the energies, we find the eigenvalues of $\hat{H}_0$:

$$\det(\hat{H}_0 - EI) = \begin{vmatrix} \frac{\hbar^2 h_z}{4} - E & 0 \\ 0 & \frac{\hbar^2 h_z}{4} - E \end{vmatrix} = \left(\frac{\hbar^2 h_z}{4} - E\right)^2 = 0 \implies E = \frac{\hbar^2 h_z}{4}. \tag{5}$$

To find the stationary states, we solve the eigenvalue equation:

$$\hat{H}_0(\alpha_\uparrow |\uparrow\rangle + \alpha_\downarrow |\downarrow\rangle) = E(\alpha_\uparrow |\uparrow\rangle + \alpha_\downarrow |\downarrow\rangle) \tag{6}$$

$$\alpha_\uparrow \frac{h_z \hbar^2}{4}|\uparrow\rangle + \alpha_\downarrow \frac{h_z \hbar^2}{4}|\downarrow\rangle = \frac{\hbar^2 h_z}{4}(\alpha_\uparrow |\uparrow\rangle + \alpha_\downarrow |\downarrow\rangle). \tag{7}$$

We see that any choice of $\alpha_\uparrow, \alpha_\downarrow$ would satisfies this eigenvalue equation and that there are two distinct eigenvectors we can form using choices of $\alpha_\uparrow, \alpha_\downarrow$. This means that there is a degeneracy and $E_1^{(0)} = E_2^{(0)} = \hbar^2 h_z/4$. To make our computations easier in the basis $\{|\uparrow\rangle, |\downarrow\rangle\}$, we will choose $\alpha_\uparrow = 1, \alpha_\downarrow = 0$ and $\alpha_\uparrow = 0, \alpha_\downarrow = 1$. Our degenerate ground states are then $|\phi_1^{(0)}\rangle = |\uparrow\rangle$ and $|\phi_2^{(0)}\rangle = |\downarrow\rangle$. The matrix elements of the Hamiltonian in the basis $\{|\phi_1^{(0)}\rangle, |\phi_2^{(0)}\rangle\}$ is,

$$[\hat{H}_0]_{\{|\phi_1^{(0)}\rangle,|\phi_2^{(0)}\rangle\}} = \begin{pmatrix} \langle\phi_1^{(0)}|\hat{H}_0|\phi_1^{(0)}\rangle & \langle\phi_1^{(0)}|\hat{H}_0|\phi_2^{(0)}\rangle \\ \langle\phi_2^{(0)}|\hat{H}_0|\phi_1^{(0)}\rangle & \langle\phi_2^{(0)}|\hat{H}_0|\phi_2^{(0)}\rangle \end{pmatrix} = \begin{pmatrix} \frac{\hbar^2 h_z}{4} & 0 \\ 0 & \frac{\hbar^2 h_z}{4} \end{pmatrix} \tag{8}$$

In order to perturb the Hamiltonian, we will need the following matrix elements (in the basis $\{|\phi_1^{(0)}\rangle, |\phi_2^{(0)}\rangle\}$):

$$[\hat{H}']_{\{|\phi_1^{(0)}\rangle,|\phi_2^{(0)}\rangle\}} = \begin{pmatrix} \langle\phi_1^{(0)}|\hat{H}'|\phi_1^{(0)}\rangle & \langle\phi_1^{(0)}|\hat{H}'|\phi_2^{(0)}\rangle \\ \langle\phi_2^{(0)}|\hat{H}'|\phi_1^{(0)}\rangle & \langle\phi_2^{(0)}|\hat{H}'|\phi_2^{(0)}\rangle \end{pmatrix} = \begin{pmatrix} 0 & -\frac{1}{2}i\lambda\hbar \\ \frac{1}{2}i\lambda\hbar & 0 \end{pmatrix}. \tag{9}$$

When calculating the first-order correction to the states, we will have to evaluate the terms $\frac{\langle\phi_2^{(0)}|\hat{H}'|\phi_1^{(0)}\rangle}{E_1^{(0)} - E_2^{(0)}}|\phi_1^{(0)}\rangle$ and $\frac{\langle\phi_1^{(0)}|\hat{H}'|\phi_2^{(0)}\rangle}{E_2^{(0)} - E_1^{(0)}}|\phi_2^{(0)}\rangle$, but because the denominators are zero, we have a problem. Our rule-of-thumb tells us though that if we can get the numerators to be zero, we can ignore these problematic terms. As we saw above, for $\hat{H}_0$, we can choose a different linear combination of eigenvectors and it will still be an eigenvector (i.e., different choice of $\alpha_\uparrow, \alpha_\downarrow$). Therefore, if we diagonalize $\hat{H}'$ so that the problematic terms are zero, $\hat{H}_0$ will be left unchanged. The eigenvectors of $\hat{H}'$ are $|\phi_a^{(0)}\rangle = \frac{1}{\sqrt{2}}\left(i\,|\uparrow\rangle + |\downarrow\rangle\right)$ and $|\phi_b^{(0)}\rangle = \frac{1}{\sqrt{2}}\left(i\,|\uparrow\rangle - |\downarrow\rangle\right)$, so if we change to the basis $\{|\phi_a^{(0)}\rangle, |\phi_b^{(0)}\rangle\}$,

$$[\hat{H}']_{\{|\phi_a^{(0)}\rangle,|\phi_b^{(0)}\rangle\}} = \begin{pmatrix} \langle\phi_a^{(0)}|\hat{H}'|\phi_a^{(0)}\rangle & \langle\phi_a^{(0)}|\hat{H}'|\phi_b^{(0)}\rangle \\ \langle\phi_b^{(0)}|\hat{H}'|\phi_a^{(0)}\rangle & \langle\phi_b^{(0)}|\hat{H}'|\phi_b^{(0)}\rangle \end{pmatrix} = \begin{pmatrix} -\frac{\lambda\hbar}{2} & 0 \\ 0 & \frac{\lambda\hbar}{2} \end{pmatrix}, \tag{10}$$

$$[\hat{H}_0]_{\{|\phi_a^{(0)}\rangle,|\phi_b^{(0)}\rangle\}} = \begin{pmatrix} \langle\phi_a^{(0)}|\hat{H}_0|\phi_a^{(0)}\rangle & \langle\phi_a^{(0)}|\hat{H}_0|\phi_b^{(0)}\rangle \\ \langle\phi_b^{(0)}|\hat{H}_0|\phi_a^{(0)}\rangle & \langle\phi_b^{(0)}|\hat{H}_0|\phi_b^{(0)}\rangle \end{pmatrix} = \begin{pmatrix} \frac{\hbar^2 h_z}{4} & 0 \\ 0 & \frac{\hbar^2 h_z}{4} \end{pmatrix}. \tag{11}$$

By changing to the eigenvector basis of $\hat{H}'$ that is also an eigenvector basis for $\hat{H}_0$, we have diagonalized both $\hat{H}'$ and $\hat{H}_0$, meaning that the off-diagonal elements (i.e., the problematic elements) of $\hat{H}'$ are zero. This means that $|\phi_a^{(0)}\rangle, |\phi_b^{(0)}\rangle$ are the "good states." We can now proceed with our calculations:

$$E_a^{(1)} = \langle\phi_a^{(0)}|\hat{H}'|\phi_a^{(0)}\rangle = -\frac{\lambda\hbar}{2} \tag{12}$$

$$E_b^{(1)} = \langle\phi_b^{(0)}|\hat{H}'|\phi_b^{(0)}\rangle = +\frac{\lambda\hbar}{2} \tag{13}$$

$$E_a^{(2)} = \sum_{m\neq a} \frac{|\langle\phi_m^{(0)}|\hat{H}'|\phi_a^{(0)}\rangle|^2}{E_m^{(0)} - E_a^{(0)}} = \cancelto{0}{\frac{|\langle\phi_b^{(0)}|\hat{H}'|\phi_a^{(0)}\rangle|^2}{E_b^{(0)} - E_a^{(0)}}} = 0 \tag{14}$$

$$E_b^{(2)} = \sum_{m\neq b} \frac{|\langle\phi_m^{(0)}|\hat{H}'|\phi_b^{(0)}\rangle|^2}{E_m^{(0)} - E_b^{(0)}} = \cancelto{0}{\frac{|\langle\phi_a^{(0)}|\hat{H}'|\phi_b^{(0)}\rangle|^2}{E_a^{(0)} - E_b^{(0)}}} = 0 \tag{15}$$

$$|\phi_a^{(1)}\rangle = \sum_{m\neq a} \frac{\langle\phi_m^{(0)}|\hat{H}'|\phi_a^{(0)}\rangle}{E_m^{(0)} - E_a^{(0)}}\,|\phi_m^{(0)}\rangle = \cancelto{0}{\frac{\langle\phi_b^{(0)}|\hat{H}'|\phi_a^{(0)}\rangle}{E_b^{(0)} - E_a^{(0)}}}\,|\phi_b^{(0)}\rangle = 0 \tag{16}$$

$$|\phi_b^{(1)}\rangle = \sum_{m\neq b} \frac{\langle\phi_m^{(0)}|\hat{H}'|\phi_b^{(0)}\rangle}{E_m^{(0)} - E_b^{(0)}}\,|\phi_m^{(0)}\rangle = \cancelto{0}{\frac{\langle\phi_a^{(0)}|\hat{H}'|\phi_b^{(0)}\rangle}{E_a^{(0)} - E_b^{(0)}}}\,|\phi_a^{(0)}\rangle = 0 \tag{17}$$

$$E_a = \frac{\hbar^2 h_z}{4} - \frac{\lambda\hbar}{2} + 0 + \cdots \tag{18}$$

$$E_b = \frac{\hbar^2 h_z}{4} + \frac{\lambda\hbar}{2} + 0 + \cdots \tag{19}$$

$$|\phi_a\rangle = |\phi_a^{(0)}\rangle + 0 + \cdots = \frac{1}{\sqrt{2}}\left(i\,|\uparrow\rangle + |\downarrow\rangle\right) + 0 + \cdots \tag{20}$$

$$|\phi_b\rangle = |\phi_b^{(0)}\rangle + 0 + \cdots = \frac{1}{\sqrt{2}}\left(i\,|\uparrow\rangle - |\downarrow\rangle\right) + 0 + \cdots \tag{21}$$

We see that there are no second-order corrections to the energies or first-order corrections to the states because of our diagonalization. However, from this process, we have obtained the resulting states that arise when the perturbation is turned on and the energy levels separate according to the first-order corrections to the energies. Now, we can calculate,

$$\langle\phi_a|\hat{S}_x|\phi_a\rangle = \left(\frac{1}{\sqrt{2}}\left(-i\,\langle\uparrow| + \langle\downarrow|\right)\right)\hat{S}_x\left(\frac{1}{\sqrt{2}}\left(i\,|\uparrow\rangle + |\downarrow\rangle\right)\right) = -\frac{\hbar}{2}, \tag{22}$$

$$\langle\phi_b|\hat{S}_x|\phi_b\rangle = \left(\frac{1}{\sqrt{2}}\left(-i\,\langle\uparrow| - \langle\downarrow|\right)\right)\hat{S}_x\left(\frac{1}{\sqrt{2}}\left(i\,|\uparrow\rangle - |\downarrow\rangle\right)\right) = \frac{\hbar}{2}, \tag{23}$$

so we see that despite there being no explicit correction to our state according to the computations, there are tangible results found by identifying the "good states."

Degenerate perturbation theory: 2×2 in a 3×3 system

Problem: Repeat what we did in the previous problem but now we consider spin-1 and

$$\hat{H}_0 = -h_z \hat{S}_z^2, \qquad \hat{H}' = \lambda(\hat{S}_x^2 + \hbar \hat{S}_x), \tag{24}$$

Solution: In the basis $\beta = \{|\uparrow\rangle, |0\rangle, |\downarrow\rangle\}$, the spin-1 operators are,

$$[\hat{S}_x]_\beta = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \qquad [\hat{S}_y]_\beta = \frac{\hbar}{i\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}, \qquad [\hat{S}_z]_\beta = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \tag{25}$$

$$[\hat{S}_z^2]_\beta = \hbar^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{26}$$

The un-perturbed and perturbing Hamiltonians in this basis are,

$$[\hat{H}_0]_\beta = h_z \hbar^2 \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \qquad [\hat{H}']_\beta = \lambda \hbar^2 \begin{pmatrix} \frac{1}{2} & \frac{1}{\sqrt{2}} & \frac{1}{2} \\ \frac{1}{\sqrt{2}} & 1 & \frac{1}{\sqrt{2}} \\ \frac{1}{2} & \frac{1}{\sqrt{2}} & \frac{1}{2} \end{pmatrix}. \tag{27}$$

We see that because $[\hat{H}_0]_\beta$ is already diagonalized, there are two degenerate stationary states $|\phi_1^{(0)}\rangle = |\uparrow\rangle$ and $|\phi_2^{(0)}\rangle = |\downarrow\rangle$ with a common energy $E_1^{(0)} = E_2^{(0)} = -h_z\hbar^2$ and another stationary state $|\phi_3^{(0)}\rangle = |0\rangle$ with energy $E_3^{(0)} = 0$. We can put the un-perturbed Hamiltonian and perturbing Hamiltonian in the new basis $\gamma = \{|\phi_1^{(0)}\rangle, |\phi_2^{(0)}\rangle, |\phi_3^{(0)}\rangle\}$, where states with common energies are grouped together:

$$[\hat{H}_0]_\gamma = h_z \hbar^2 \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \qquad [\hat{H}']_\gamma = \lambda \hbar^2 \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & \frac{1}{\sqrt{2}} \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 1 \end{pmatrix}. \tag{28}$$

Note the matrix representations for an operator A in the bases β, γ are related by $[A]_\gamma = O_{\beta\gamma}^\dagger [A]_\beta O_{\beta\gamma}$ where $O_{\beta\gamma} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$. The 2×2 block in the upper left of matrices $[\hat{H}_0]_\gamma$ and $[\hat{H}']_\gamma$ is known as the 'degenerate block' with energy $E_1^{(0)} = E_2^{(0)} = -h_z\hbar^2$. In order to perform perturbation theory and not have to deal with terms that blow up, we need the terms on the off-diagonal within the degenerate block to be zero. This is done by forming appropriate linear combinations of the basis states $|\phi_1^{(0)}\rangle$ and $|\phi_2^{(0)}\rangle$ that diagonalize the 2×2 block. To perform the diagonalization, we find the eigenvectors of the 2×2 block: $\frac{\lambda\hbar^2}{2} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$. The eigenvectors of the block are $\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$ and $\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$ which can be found by finding the eigenvalues then solving the eigenvector equation. This tells us that our new basis vectors should be chosen so that $|\phi_1^{(0)}\rangle$ and $|\phi_2^{(0)}\rangle$ are replaced with $|\phi_a^{(0)}\rangle = \frac{1}{\sqrt{2}}(|\phi_1^{(0)}\rangle + |\phi_2^{(0)}\rangle)$ and $|\phi_b^{(0)}\rangle = \frac{1}{\sqrt{2}}(|\phi_1^{(0)}\rangle - |\phi_2^{(0)}\rangle)$. We call this new basis $\eta = \{|\phi_a^{(0)}\rangle, |\phi_b^{(0)}\rangle, |\phi_3^{(0)}\rangle\}$. The change-of-basis matrix is,

$$O_{\gamma\eta} = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{29}$$

so in the new basis the un-perturbed and perturbing Hamiltonians are,

$$[\hat{H}_0]_\eta = O_{\gamma\eta}^\dagger [\hat{H}_0]_\gamma O_{\gamma\eta} = \hbar^2 h_z \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} \langle\phi_a^{(0)}|\hat{H}_0|\phi_a^{(0)}\rangle & \langle\phi_a^{(0)}|\hat{H}_0|\phi_b^{(0)}\rangle & \langle\phi_a^{(0)}|\hat{H}_0|\phi_3^{(0)}\rangle \\ \langle\phi_b^{(0)}|\hat{H}_0|\phi_a^{(0)}\rangle & \langle\phi_b^{(0)}|\hat{H}_0|\phi_b^{(0)}\rangle & \langle\phi_b^{(0)}|\hat{H}_0|\phi_3^{(0)}\rangle \\ \langle\phi_3^{(0)}|\hat{H}_0|\phi_a^{(0)}\rangle & \langle\phi_3^{(0)}|\hat{H}_0|\phi_b^{(0)}\rangle & \langle\phi_3^{(0)}|\hat{H}_0|\phi_3^{(0)}\rangle \end{pmatrix}, \tag{30}$$

$$[\hat{H}']_\eta = O_{\gamma\eta}^\dagger [\hat{H}']_\gamma O_{\gamma\eta} = \lambda\hbar^2 \begin{pmatrix} 1 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 1 \end{pmatrix} = \begin{pmatrix} \langle\phi_a^{(0)}|\hat{H}'|\phi_a^{(0)}\rangle & \langle\phi_a^{(0)}|\hat{H}'|\phi_b^{(0)}\rangle & \langle\phi_a^{(0)}|\hat{H}'|\phi_3^{(0)}\rangle \\ \langle\phi_b^{(0)}|\hat{H}'|\phi_a^{(0)}\rangle & \langle\phi_b^{(0)}|\hat{H}'|\phi_b^{(0)}\rangle & \langle\phi_b^{(0)}|\hat{H}'|\phi_3^{(0)}\rangle \\ \langle\phi_3^{(0)}|\hat{H}'|\phi_a^{(0)}\rangle & \langle\phi_3^{(0)}|\hat{H}'|\phi_b^{(0)}\rangle & \langle\phi_3^{(0)}|\hat{H}'|\phi_3^{(0)}\rangle \end{pmatrix}. \tag{31}$$

We see that by changing to the new basis η, we have made the off-diagonal elements of the 2×2 degenerate block all zero so that we may proceed with the perturbation theory calculation. I have written out what each matrix entry represents as a matrix elements on the RHS of the above equations in order to make what we're doing and how it relates to the computations a bit more explicit. Now, we can proceed with the perturbation theory calculation:

$$E_a^{(1)} = \langle \phi_a^{(0)} | \hat{H}' | \phi_a^{(0)} \rangle = \lambda\hbar^2 \tag{32}$$

$$E_b^{(1)} = \langle \phi_b^{(0)} | \hat{H}' | \phi_b^{(0)} \rangle = 0 \tag{33}$$

$$E_3^{(1)} = \langle \phi_3^{(0)} | \hat{H}' | \phi_3^{(0)} \rangle = \lambda\hbar^2 \tag{34}$$

$$E_a^{(2)} = \sum_{m \neq a} \frac{|\langle \phi_m^{(0)} | \hat{H}' | \phi_a^{(0)} \rangle|^2}{E_a^{(0)} - E_m^{(0)}} = \cancelto{0}{\frac{|\langle \phi_b^{(0)} | \hat{H}' | \phi_a^{(0)} \rangle|^2}{E_a^{(0)} - E_b^{(0)}}} + \frac{\lambda\hbar^2}{-\hbar^2 h_z} = -\frac{\lambda^2\hbar^2}{h_z} \tag{35}$$

$$E_b^{(2)} = \sum_{m \neq b} \frac{\langle| \phi_m^{(0)} | \hat{H}' | \phi_b^{(0)} \rangle|^2}{E_b^{(0)} - E_m^{(0)}} = \cancelto{0}{\frac{|\langle \phi_a^{(0)} | \hat{H}' | \phi_b^{(0)} \rangle|^2}{E_b^{(0)} - E_a^{(0)}}} + 0 = 0 \tag{36}$$

$$E_3^{(2)} = \sum_{m \neq 3} \frac{|\langle \phi_m^{(0)} | \hat{H}' | \phi_3^{(0)} \rangle|^2}{E_3^{(0)} - E_m^{(0)}} = \frac{\lambda^2\hbar^4}{\hbar^2 h_z} + 0 = +\frac{\lambda^2\hbar^2}{h_z} \tag{37}$$

$$|\phi_a^{(1)}\rangle = \sum_{m \neq a} \frac{\langle \phi_m^{(0)} | \hat{H}' | \phi_a^{(0)} \rangle}{E_a^{(0)} - E_m^{(0)}} |\phi_m^{(0)}\rangle = \cancelto{0}{\frac{\langle \phi_b^{(0)} | \hat{H}' | \phi_a^{(0)} \rangle}{E_a^{(0)} - E_b^{(0)}}} |\phi_b^{(0)}\rangle - \frac{\lambda\hbar^2}{\hbar^2 h_z} |\phi_3^{(0)}\rangle = -\frac{\lambda}{h_z} |0\rangle \tag{38}$$

$$|\phi_b^{(1)}\rangle = \sum_{m \neq b} \frac{\langle \phi_m^{(0)} | \hat{H}' | \phi_b^{(0)} \rangle}{E_b^{(0)} - E_m^{(0)}} |\phi_m^{(0)}\rangle = \cancelto{0}{\frac{\langle \phi_a^{(0)} | \hat{H}' | \phi_b^{(0)} \rangle}{E_b^{(0)} - E_a^{(0)}}} |\phi_a^{(0)}\rangle + 0 = 0 \tag{39}$$

$$|\phi_3^{(1)}\rangle = \sum_{m \neq 3} \frac{\langle \phi_m^{(0)} | \hat{H}' | \phi_3^{(0)} \rangle}{E_3^{(0)} - E_m^{(0)}} |\phi_m^{(0)}\rangle = \frac{\lambda\hbar^2}{\hbar^2 h_z} |\phi_a^{(0)}\rangle + 0 = \frac{\lambda}{h_z}\frac{1}{\sqrt{2}}(|\uparrow\rangle + |\downarrow\rangle). \tag{40}$$

Putting this all together,

$$|\phi_a\rangle = |\phi_a^{(0)}\rangle + |\phi_a^{(1)}\rangle + \cdots = \frac{1}{\sqrt{2}}(|\uparrow\rangle + |\downarrow\rangle) - \frac{\lambda}{h_z}|0\rangle + \cdots \tag{41}$$

$$|\phi_b\rangle = |\phi_b^{(0)}\rangle + |\phi_b^{(1)}\rangle + \cdots = \frac{1}{\sqrt{2}}(|\uparrow\rangle - |\downarrow\rangle) + 0 + \cdots \tag{42}$$

$$|\phi_3\rangle = |\phi_3^{(0)}\rangle + |\phi_3^{(1)}\rangle + \cdots = |0\rangle + \frac{\lambda}{h_z\sqrt{2}}(|\uparrow\rangle + |\downarrow\rangle) + \cdots \tag{43}$$

$$E_a = E_a^{(0)} + E_a^{(1)} + E_a^{(2)} + = -\hbar^2 h_z + \lambda\hbar^2 - \lambda^2\frac{\hbar^2}{h_z} \cdots \tag{44}$$

$$E_b = E_b^{(0)} + E_b^{(1)} + E_b^{(2)} + \cdots = -\hbar^2 h_z + 0 + 0 + \cdots \tag{45}$$

$$E_3 = E_3^{(0)} + E_3^{(1)} + E_3^{(2)} + \cdots = 0 + \lambda\hbar^2 + \lambda^2\frac{\hbar^2}{h_z} + \cdots \tag{46}$$

To first order, the expected x-magnetizations are:

$$\langle \phi_a | \hat{S}_x | \phi_a \rangle = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{\lambda}{h_z} \\ \frac{1}{\sqrt{2}} \end{pmatrix}^\dagger \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{\lambda}{h_z} \\ \frac{1}{\sqrt{2}} \end{pmatrix} = -2\hbar(\lambda/\hbar) \tag{47}$$

$$\langle \phi_b | \hat{S}_x | \phi_b \rangle = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ 0 \\ -\frac{1}{\sqrt{2}} \end{pmatrix}^\dagger \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}} \\ 0 \\ -\frac{1}{\sqrt{2}} \end{pmatrix} = 0 \tag{48}$$

$$\langle \phi_3 | \hat{S}_x | \phi_3 \rangle = \begin{pmatrix} \frac{\lambda}{\sqrt{2}h_z} \\ 1 \\ \frac{\lambda}{\sqrt{2}h_z} \end{pmatrix}^\dagger \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} \frac{\lambda}{\sqrt{2}h_z} \\ 1 \\ \frac{\lambda}{\sqrt{2}h_z} \end{pmatrix} = 2\hbar(\lambda/\hbar) \tag{49}$$

Variational method and the radial equation

Problem: Consider the 3D system of a particle in a isotropic, central, quadratic potential $V(r) = \alpha r^2$ so that its Hamiltonian is,

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \alpha r^2. \tag{50}$$

Provide an ansatz, apply the variational method, and find an upper bound on the ground state energy.

Reminder: When we solve the time-independent Schrödinger equation with a spherically-symmetric potential, we use separation of variables, write $\psi(r,\theta,\phi) = Y_\ell^m(\theta,\phi)R(r)$, and arrive at the equation,

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{\hbar^2\ell(\ell+1)}{2mr^2} + V(r)\right]u(r) = Eu(r), \tag{51}$$

where $u(r) = rR(r)$. This is the 'reduced radial equation' and can be found in Griffiths in the section titled *Radial equation*. This means that,

$$\hat{H}[Y_\ell^m(\theta,\phi)u(r)r^{-1}] = \left[-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \frac{\hbar^2\ell(\ell+1)}{2mr^2}u(r) + V(r)u(r)\right]Y_\ell^m(\theta,\phi)r^{-1}. \tag{52}$$

Also, remember the following about the spherical harmonics:

$$\int_0^\pi\int_0^{2\pi} Y_{\ell_2}^{m_2}(\theta,\phi)^* Y_{\ell_1}^{m_1}(\theta,\phi)d\theta d\phi = \delta_{\ell_1\ell_2}\delta_{m_1m_2} \tag{53}$$

$$Y_0^0(\theta,\phi) = \frac{1}{2\sqrt{\pi}}. \tag{54}$$

Therefore, if the wave-function is of the form $\psi(r,\theta,\phi) = Y_\ell^m u(r)r^{-1}$, the normalization condition becomes,

$$1 = \int_0^\infty\int_0^{2\pi}\int_0^\pi \psi^*\psi r^2\sin\theta d\theta d\phi dr = \left(\int_0^\pi\int_0^{2\pi}|Y_\ell^m(\theta,\phi)|^2\sin\theta d\theta d\phi\right)\left(\int_0^\infty [r^{-1}u(r)]^* r^{-1}u(r)r^2dr\right) = \int_0^\infty |u(r)|^2dr. \tag{55}$$

Solution: Using the radial equation, we see that if we choose ansatzes of the form $\psi(r,\theta,\phi) = Y_\ell^m(\theta,\phi)u(r)r^{-1}$, computations become significantly easier. Therefore, as an example, we will choose $u_a(r) = Ae^{-ar^2}$ where A is a normalization constant and a is a variational parameter. Additionally, we will find a state with zero angular momentum: $\ell = 0$. This makes the 'whole' ansatz $\psi_a(r,\theta,\phi) = AY_0^0(\theta,\phi)e^{-ar^2}r^{-1} = Ar^{-1}e^{-ar^2}/(2\sqrt{\pi})$. Going through our usual variational method procedure, first we normalize:

$$1 = \iiint |\psi_a|^2 dV = \int_0^\infty |u_a(r)|^2dr = A^2\int_0^\infty e^{-2ar^2}dr = A^2\frac{1}{2}\sqrt{\frac{\pi}{2a}} \implies A = \left(\frac{8a}{\pi}\right)^{1/4}, \tag{56}$$

where we have used the formula $\int_{-\infty}^\infty e^{-bx^2}dx = \sqrt{\pi/b}$. Next we compute the Hamiltonian acting on the ansatz according to equation 52,

$$\begin{aligned}
\hat{H}[\psi_a] &= AY_0^0(\theta,\phi)r^{-1}\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}e^{-ar^2} + \frac{\hbar^2 0(0+1)}{2mr^2}e^{-ar^2} + \alpha r^2e^{-ar^2}\right] \\
&= AY_0^0(\theta,\phi)r^{-1}\left[-\frac{\hbar^2}{2m}\left[4a^2r^2e^{-ar^2} - 2ae^{-ar^2}\right] + \frac{\hbar^2 0(0+1)}{2mr^2}e^{-ar^2} + \alpha r^2e^{-ar^2}\right] \\
&= AY_0^0(\theta,\phi)r^{-1}\left[\left(\alpha - \frac{2\hbar^2a^2}{m}\right)r^2e^{-ar^2} + \frac{\hbar^2a}{m}e^{-ar^2}\right].
\end{aligned} \tag{57}$$

Next, we compute the expected energy,

$$\begin{aligned}
\langle\psi_a|\hat{H}|\psi_a\rangle &= \int_0^{2\pi}\int_0^\pi\int_0^\infty \psi_a^*\hat{H}[\psi_a]r^2\sin\theta drd\theta d\phi \\
&= A^2\cancelto{1}{\iint|Y_0^0(\theta,\phi)|^2d\Omega}\int_0^\infty r^{-1}e^{-ar^2}r^{-1}\left[\left(\alpha - \frac{2\hbar^2a^2}{m}\right)r^2e^{-ar^2} + \frac{\hbar^2a}{m}e^{-ar^2}\right]r^2dr \\
&= A^2\left[\left(\alpha - \frac{2\hbar^2a^2}{m}\right)\int_0^\infty r^2e^{-2ar^2}dr + \frac{\hbar^2a}{m}\int_0^\infty e^{-2ar^2}dr\right].
\end{aligned}$$

To calculate these integrals we use integration by parts,

$$\frac{d}{dr} r e^{-2ar^2} = e^{-2ar^2} - 4ar^2 e^{-2ar^2} \implies r e^{-2ar^2}\Big|_{r=0}^{r\to\infty} = \int_0^\infty e^{-2ar^2}\,dr - 4a\int_0^\infty r^2 e^{-2ar^2}\,dr$$
$$0 = \frac{1}{2}\sqrt{\frac{\pi}{2a}} - 4a\int_0^\infty r^2 e^{-2ar^2}\,dr \implies \int_0^\infty r^2 e^{-2ar^2}\,dr = \frac{1}{8}\sqrt{\frac{\pi}{2a^3}}. \tag{58}$$

Therefore,

$$\langle\psi_a|\hat{H}|\psi_a\rangle = A^2\left[\left(\alpha - \frac{2\hbar^2 a^2}{m}\right)\frac{1}{8}\sqrt{\frac{\pi}{2a^3}} + \frac{\hbar^2 a}{m}\frac{1}{8}\sqrt{\frac{\pi}{2a^3}}\right] = A^2\sqrt{\frac{\pi}{2}}\left(\frac{\alpha}{8a^{3/2}} + \frac{\sqrt{a}\hbar^2}{4m}\right) = \frac{\alpha}{4a} + \frac{a\hbar^2}{2m}. \tag{59}$$

Next, we minimize this by computing stationary points of $\langle\psi_a|\hat{H}|\psi_a\rangle$ with respect to a:

$$\frac{\partial}{\partial a}\langle\psi_a|\hat{H}|\psi_a\rangle = \frac{\hbar^2}{2m} - \frac{\alpha}{4a^2} = 0 \implies \frac{a^2\hbar^2}{2m} - \frac{\alpha}{4} = 0 \implies a = \pm\sqrt{\frac{m\alpha}{2\hbar^2}}. \tag{60}$$

We must have $a^\star = \sqrt{m\alpha/(2\hbar^2)}$ because if $a^\star$ were negative, the ansatz would not be normalizable. Plugging this back into the average energy (line 59), the variational energy is,

$$\langle\psi_a|\hat{H}|\psi_a\rangle = \sqrt{\frac{\alpha\hbar^2}{2m}}. \tag{61}$$