Collaborators

I worked with **Andrew Binder** to complete this assignment.

Problem 1

Let **a**, and **b** be two constant vectors. Show that

$$\int (\mathbf{a}\cdot\hat{r})(\mathbf{b}\cdot\hat{r})\sin\theta d\theta d\phi = \frac{4\pi}{3}(\mathbf{a}\cdot\mathbf{b})$$

(the integration is over the usual range: $0<\theta<\pi, 0<\phi<2\pi$). Use this result to demonstrate that

$$\left\langle \frac{3(\mathbf{S}_p\cdot r)(\mathbf{S}_e\cdot r)-\mathbf{S}_p\mathbf{S}_e}{r^3}\right\rangle = 0$$

for states with $l=0$. *Hint:* $\hat{r}=\sin\theta\cos\phi\hat{i}+\sin\theta\sin\phi\hat{j}+\cos\theta\hat{k}$. Do the angular integrals first.

Solution: To do this, we write our vectors in spherical coordinates. After some algebra, we get that the integral is the same as evaluating:

$$\int (\mathbf{a}\cdot\hat{r})(\mathbf{b}\cdot\hat{r})\sin\theta d\theta d\phi = \int (a_xb_x\sin^2\theta\cos^2\phi + a_yb_y\sin^2\theta\sin^2\phi + a_zb_z\cos^2\theta)\cdot\sin\theta d\theta d\phi$$

(Note that here I've already killed the terms which give us 0 when integrating from 0 to 2π.) This final integral is independent of ϕ, so the integral $\int d\phi = 2\pi$. Therefore, we integrate from $0<\theta<\pi$:

$$\begin{aligned}\int (\mathbf{a}\cdot\hat{r})(\mathbf{b}\cdot\hat{r})\sin\theta d\theta d\phi &= \int_0^\pi a_xb_x\pi\sin^3\theta + a_yb_y\pi\sin^3\theta + 2\pi a_zb_z\cos^2\theta\sin\theta d\theta \\ &= \pi a_xb_x\int_0^\pi \sin^3\theta d\theta + \pi a_yb_y\int_0^\pi\sin^3\theta d\theta + 2\pi a_zb_z\int_0^\pi\cos^2\theta\sin\theta d\theta \\ &= \frac{4\pi}{3}a_xb_x + \frac{4\pi}{3}a_yb_y + \frac{4\pi}{3}a_zb_z = \frac{4\pi}{3}(\mathbf{a}\cdot\mathbf{b})\end{aligned}$$

as desired. Now evaluating the expectation value, we first notice that the spin components are independent of r, so this is actually the product of two separate integrals. Also, $Y_{00}=\frac{1}{\sqrt{4\pi}}$ which is a constant, so combining these two we get:

$$\left\langle \frac{3(\mathbf{S}_p\cdot r)(\mathbf{S}_e\cdot r)-\mathbf{S}_p\mathbf{S}_e}{r^3}\right\rangle = \int\frac{1}{r^3}R_{n0}dr\cdot\frac{1}{4\pi}\int 3(\mathbf{S}_p\cdot r)(\mathbf{S}_e\cdot r)-\mathbf{S}_p\mathbf{S}_e d\theta d\phi$$

Now using the identity we just derived, we get:

$$\int\frac{1}{r^3}R_{n0}dr\cdot\frac{1}{4\pi}\int 3(\mathbf{S}_p\cdot r)(\mathbf{S}_e\cdot r)-\mathbf{S}_p\mathbf{S}_e d\theta d\phi = \int\frac{R_{n0}}{r^3}dr\cdot\frac{1}{4\pi}\int(3(\mathbf{S}_p\cdot r)(\mathbf{S}_e\cdot r)-\mathbf{S}_p\mathbf{S}_e)\sin\theta d\theta d\phi$$

Now we focus on the angular integral. The first term can be calculated using our identity:

$$\frac{1}{4\pi}\int 3(\mathbf{S}_p\cdot r)(\mathbf{S}_e\cdot r) = \frac{3}{4\pi}\frac{4\pi}{3}\mathbf{S}_p\mathbf{S}_e = \mathbf{S}_p\mathbf{S}_e$$

Then, since the proton and electron spin are constant, then we can pull $\mathbf{S}_p\mathbf{S}_e$ out of the integral, giving us:

$$\begin{aligned}\frac{1}{4\pi}\int \mathbf{S}_p\mathbf{S}_e \sin\theta d\theta d\phi &= \mathbf{S}_p\mathbf{S}_e \int \sin\theta d\theta d\phi \\ &= \frac{1}{4\pi}\mathbf{S_p}\mathbf{S}_e(4\pi) \\ &= \mathbf{S}_p\mathbf{S}_e\end{aligned}$$

So combining these two terms, we get:

$$\frac{1}{4\pi}\int (3(\mathbf{S}_p \cdot r)(\mathbf{S}_e \cdot r) - \mathbf{S}_p\mathbf{S}_e) \sin\theta d\theta d\phi = \mathbf{S}_p\mathbf{S}_e - \mathbf{S}_p\mathbf{S}_e = 0$$

as desired. $\square$

Problem 2

When an atom is placed in a uniform external electric field $\mathbf{E}_{ext}$, the energy levels are shifted – a phenomenon known as the **Stark effect** (it is the electrical analog to the Zeeman effect). In this problem we analyze the Stark effect for the $n = 1$ and $n = 2$ states of hydrogen. Let the field point in the z direction, so the potential energy of the electron is

$$H'_s = eE_{ext}z = eE_{ext}r\cos\theta$$

Treat this as a phemonenon as a perturbation of the Bohr Hamiltonian (Equation 7.43). (Spin is irrelevant to this problem, so ignore it, and neglect the fine structure.)

(a) Show that the ground state energy is not affected by this perturbation, in first order.

Solution: The integral to first order is:

$$\langle nlm|z|nlm\rangle$$

which is an integral over an even interval of an odd function, so therefore it's zero. □

(b) Show that the ground state is four-fold degenerate: $\psi_{200}, \psi_{211}, \psi_{210}, \psi_{21-1}$. Using degenerate perturbation theory, determine the first-order corrections to the energy. Into how many levels does E_2 split?

Solution: The energy in this case is only a function of n, and since these four states (which are also the only allowable states for $n = 2$) share the same value of n, they are degenerate. Calculating the diagonal matrix elements (and skipping the algebra), we get:

$$\begin{aligned}
\langle 200|H|200\rangle &= 0\\
\langle 211|H|211\rangle &= 0\\
\langle 210|H|210\rangle &= 0\\
\langle 21-1|H|21-1\rangle &= 0
\end{aligned}$$

Now for the off-diagonal terms, I abuse symmetry so I only compute half of them:

$$\begin{aligned}
\langle 200|H|211\rangle &= 0\\
\langle 200|H|210\rangle &= -3a_0\\
\langle 200|H|21-1\rangle &= 0\\
\langle 211|H|210\rangle &= 0\\
\langle 211|H|21-1\rangle &= 0\\
\langle 210|H|21-1\rangle &= 0
\end{aligned}$$

So constructing the full H' we have:

$$H' = eE\begin{pmatrix} 0 & 0 & -3a_0 & 0\\ 0 & 0 & 0 & 0\\ -3a_0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\end{pmatrix}$$

The eigenvalues of this matrix (which i did via a computer, I'm lazy, and I don't want to type it out) are $\lambda = 0, \pm 3a_0$, with eiegenvectors $|211\rangle, |21-1\rangle, \frac{1}{\sqrt{2}}(|200\rangle \pm |210\rangle)$. The first two states have an energy correction of 0, and the last two are split by a difference of $6eEa_0$. Therefore, the perturbation splits the degeneracy into three energy levels, with two states in $E = E_2$ and the other two with $E = E_2 \pm 3eEa_0$. $\square$

(c) What are the "good" wave functions for part (b)? Find the expectation value of the electric dipole moment ($\mathbf{p}_e = -e\mathbf{r}$), in each of these "good" states. Notice that the results are independent of the applied field – evidently hydrogen in its first excited state can carry a *permanent* electric dipole moment.

Solution: As mentioned in the previous problem, the "good" wave functions are: $|211\rangle, |21-1\rangle$, $\frac{1}{\sqrt{2}}(|200\rangle \pm |210\rangle)$. To calcute the electric dipole moment, we notice that $\langle \mathbf{p} \rangle = -e\langle r \rangle$. For the two unchanged states $|211\rangle$ and $|21-1\rangle$, we have $\langle r \rangle = 0$, so we have $\langle \mathbf{p} \rangle = 0$ for those states too. Calculating the expectation value for the other term, we have:

$$\langle r \rangle = \int \frac{1}{2}(R_{20}^* Y_{00} \pm R_{21}^* \sqrt{3}\cos\theta Y_{00}^*)(R_{20}Y_{00} \pm R_{21}\sqrt{3}\cos\theta Y_{00})$$

Expanding this out, we get that the non-cross terms evaluate to 0, so this integral becomes:

$$\langle r \rangle = \frac{1}{2}\left[\int R_{20}R_{21}^* |Y_{00}|^2 \cdot 3 \cdot \cos^2\theta r^3 \sin\theta dr d\theta d\phi \pm \int R_{20}^* R_{21} |Y_{00}|^2 \cdot 3 \cdot \cos^2\theta r^3 \sin\theta d\theta d\phi\right]$$

And since R_{20} and R_{21} are real quantities, then this integral simplifies even further:

$$\langle r \rangle = \pm\frac{3}{4\pi}\int R_{20}R_{21}\cos^2\theta \sin\theta r^3 dr d\theta d\phi$$

The θ integral gives $2/3$ and the ϕ integral gives 2π, so therefore:

$$\begin{aligned}
\langle r \rangle &= \pm\int_0^\infty R_{21}R_{20}r^3 dr d\theta d\phi \\
&= \pm\frac{a^{-3}}{2\sqrt{12}}\int_0^\infty r^2\left(\frac{r}{a} - \frac{r^2}{2a^2}\right)e^{-r/a}dr \\
&= \pm\frac{a^{-3}}{2\sqrt{12}}\left(24a^4 - 60a^4\right) \\
&= \pm\frac{36a}{2\sqrt{12}} \\
&= 3\sqrt{3}a
\end{aligned}$$

So therefore, the expectation value of the dipole moment that we get is $\langle \mathbf{p} \rangle = 3\sqrt{3}ea$. $\square$

Problem 3

Calculate the wavelength, in centimeters, of the photon emitted uner a hyperfine transition in the ground state ($n = 1$) of **deuterium**. Deuterium is "heavy" hydrogen, with an extra neutron in the nucleus; the proton and neutron bind together to form a **deuteron**, with spin 1 and magnetic moment

$$\mu_d = \frac{g_d e}{2m_d}\mathbf{S}_d$$

the deutron g-factor is 1.71.

Solution: We use the same formulas, except we replace $\mathbf{S}_p$ wiht $\mathbf{S}_d$. Writing out the Hyperfine correction, we have:

$$H'_{hf} = \frac{\mu_0 g_d e^2}{2m_d m_e}\langle \mathbf{S}_d \cdot \mathbf{S}_e \rangle = \frac{\mu_0 g_d e^2}{3m_d m_e} \cdot \frac{1}{2}(S_T^2 - S_e^2 - S_d^2)$$

The electron has spin 1/2, so therefore $S_e^2 = 3/4\hbar^2$. The deuteron has spin 1, so $S_d^2 = (1)(2)\hbar^2 = 2\hbar^2$. There are two possible cases for the total spin: $S_T = 1/2$ and $S_T = 3/2$. This gives the values $S_T^2 = 3/4\hbar^2$ or $S_T^2 = 15/4\hbar^2$ respectively. Since S_d and S_e are the same for both energy states, the energy difference really just comes from the difference in the S_T term. Therefore:

$$\begin{aligned}
\Delta E &= \frac{\mu_0 g_d e^2}{3\pi m_d m_e a^3 \pi} \cdot \frac{1}{2}\left(\frac{15}{4} - \frac{3}{4}\right)\hbar^2 \\
&= \frac{\mu_0 g_d e^2}{2m_d m_e a^3 \pi} \cdot \frac{3}{2}\hbar^2 \\
&= \frac{\mu_0 g_d e^2 \hbar^2}{2m_d m_e a^3 \pi}
\end{aligned}$$

Finally, the wavelength can be calculated as $\lambda = c/v = hc/\Delta E$, so plugging what we have in, we get:

$$\lambda = \frac{4\pi m_d m_e a^3}{\mu_0 g_d e^2 \hbar} \approx 91.88 \text{ cm}$$

$\square$

Problem 4

(a) Prove the following corollary to the variational principle: If $\langle\psi|\psi_{gs}\rangle = 0$, then $\langle H\rangle \geq E_{fe}$, where E_{fe} is the energy of the first excited state. *Comment:* If we can find a trial function that is orthogonal to the exact ground state, we can get an upper bound on the *first excited state*. In general, it's difficult to be sure that ψ is orthogonal to ψ_{gs}, since (presumably) we don't *know* the latter. However, if the potential $V(x)$ is a fnction of x, then the ground state is likewise even, and hence any *odd* trial function will automatically meet the condition for the corollary.

Solution: Consider the representation of ψ in its basis expansion:

$$\psi = \sum_{n=0}^{\infty} c_n\psi_n$$

where

$$c_n = \langle\psi_n|\psi\rangle$$

If $\langle\psi|\psi_{gs}\rangle = 0$, then this means that $c_0 = 0$, so we can rewrite our sum as:

$$\psi = \sum_{n=1}^{\infty} c_n\psi_n$$

The minimum possible energy for a state written in this form is obviously E_{fe} (this is done by setting all but c_1 equal to zero), which proves the corollary. More explicilty, we can write $\langle H\rangle$ as:

$$\langle H\rangle = \sum_{n=1}^{\infty} E_n|c_n|^2 \geq \sum_{n=1}^{\infty} E_{fe}|c_n|^2$$

And since E_{fe} is a constant, then we can pull it out, which gives:

$$\langle H\rangle \geq E_{fe}\sum_{n=1}^{\infty}|c_n|^2 = E_{fe}$$

as desired. □

(b) Find the best bound on the first excited state of the one-dimensional harmonic oscillator using the trial function

$$\psi(x) = Axe^{-bx^2}$$

Solution: First, we can find A by normalization:

$$1 = |A|^2\int_{-\infty}^{\infty} x^2e^{-2bx^2}dx$$

which we can do with the help of a computer:

$$|A|^2 = \sqrt{\frac{32b^3}{\pi}} \implies A = \sqrt[4]{\frac{32b^3}{\pi}}$$

With this determined, we can calculate $\langle H\rangle$:

$$\begin{aligned}\langle H\rangle &= \int_{-\infty}^{\infty} Axe^{-bx^2}\left(-\frac{\hbar}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2x^2\right)Axe^{-bx^2}dx \\ &= -\frac{|A|^2\hbar}{2m}\int_{-\infty}^{\infty} xe^{-bx^2}(2bxe^{-bx^2} + 4b^2x^3e^{-bx^2})dx + \frac{m\omega^2|A|^2}{2}\int_{-\infty}^{\infty} x^2e^{-2bx^2}\cdot x^2dx\end{aligned}$$

Now abusing the power of WolframAlpha, we get:

$$\langle H \rangle = \frac{3\hbar^2 b}{2m} + \frac{3m\omega^2}{8b}$$

To find the best bound, we take $\frac{\partial \langle H \rangle}{\partial b}$, which gives:

$$\frac{\partial \langle H \rangle}{\partial b} = 0 = \frac{3\hbar^2}{2m} - \frac{3m\omega^2}{8b^2}$$
$$\therefore b^2 = \frac{m^2\omega^2}{4\hbar^2} \implies b = \frac{m\omega}{2\hbar}$$

Plugging this value of b back:

$$\langle H \rangle_{min} = \frac{3\hbar^2}{2m}\left(\frac{m\omega}{2\hbar}\right) + \frac{3m\omega^2}{8\left(\frac{m\omega}{2\hbar}\right)} = \frac{3}{2}\hbar\omega$$

$\square$

Problem 5

Find the lowest bound on the ground state of hydrogen you can get using a gaussian trial wave function

$$\psi(r) = Ae^{-br^2}$$

where A is determined by normalization and b is an adjustable parameter. *Answer:* -11.5 eV.

Solution: Computing the normalization constant first:

$$1 = |A|^2 \int_{-\infty}^{\infty} e^{-2br^2} r^2 \sin\theta dr d\theta d\phi$$

Again abusing Wolfram:

$$1 = |A|^2 \left(\frac{\pi}{2b}\right)^{3/2} \implies A = \left(\frac{2b}{\pi}\right)^{3/4}$$

Now calculating $\langle H \rangle$:

$$\begin{aligned}
\langle H \rangle &= \int Ae^{-br^2} \left(\frac{-\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}\right) Ae^{-br^2} dV \\
&= \frac{|A|^2\hbar^2}{2m} \int Ae^{-br^2} \left(\nabla^2 e^{-br^2}\right) - \frac{|A|^2 e^2}{4\pi\epsilon_0} \int e^{-br^2} \frac{1}{r} e^{-br^2} dV \\
&= \frac{|A|^2\hbar^2}{2m} \int e^{-br^2} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \cdot -2bre^{-br^2}\right) dV - \frac{|A|^2 e^2}{4\pi\epsilon_0} \int \frac{1}{r} e^{-2br^2} dV
\end{aligned}$$

The integral over θ gives us 2, and the integral over ϕ gives us 2π. Thus, we're left only with the radial portion, which after evaluating the Laplacian is:

$$\langle H \rangle = \frac{A^2\hbar^2}{m}(4\pi) \int_0^{\infty} e^{-br^2} \left(-6br^2 e^{-br^2} + 4r^4 b^2 e^{-br^2}\right) dr - \frac{|A|^2 e^2}{\epsilon_0} \int_0^{\infty} re^{-2br^2} dr$$

Again, using the power of WolframAlpha we get:

$$\langle H \rangle = \frac{3\hbar^2 b}{2m} - \frac{e^2}{2\pi\epsilon_0}\sqrt{\frac{2b}{\pi}}$$

Taking the derivative with respect to b, we get:

$$\frac{\partial \langle H \rangle}{\partial b} = 0 = \frac{3\hbar^2}{2m} - \frac{e^2}{4\pi\epsilon_0}\sqrt{\frac{2}{\pi}}\frac{1}{2\sqrt{b}} \implies b = \frac{e^4 m^2}{18\pi^3\epsilon_0^2\hbar^4}$$

Plugging this back in, we get:

$$\langle H \rangle_{min} = \frac{3\hbar^2}{2m}\left(\frac{e^4 m^2}{18\pi^3\epsilon_0^2\hbar^4}\right) - \frac{e^2}{2\pi\epsilon_0}\sqrt{\frac{2}{\pi}}\left(\frac{me^2}{\epsilon_0\hbar^2}\sqrt{\frac{1}{18\pi^3}}\right) \approx -11.5 \text{ eV}$$

□

Problem 6

Apply the Rayleigh-Ritz variational method to a particle in a box of width L to find the ground state energy using a second degree polynomial as a trial wave function.

Solution: We need to select our trial wavefunction to satisfy the condition that $\psi(0) = 0$ and $\psi(L) = 0$, so then we must have:

$$\psi = Ax(L - x)$$

as our second-degree trial function. Computing the normalization constant, we have:

$$1 = |A|^2 \int_0^L x^2(L - x)^2 dx$$

which through the power of a computer we get:

$$1 = A^2 \frac{L^5}{30} \implies A = \sqrt{\frac{30}{L^5}}$$

Now we can find $\langle H \rangle$:

$$\begin{aligned}
\langle H \rangle &= -\frac{\hbar^2}{2m} A^2 \int_0^L x(L - x) \frac{\partial^2}{\partial x^2} \left(x(L - x) \right) dx \\
&= A^2 \int_0^L x(L - x)(-2) dx \\
&= -\frac{\hbar^2 A^2}{2m} \left(-\frac{L^3}{3} \right) \\
&= -\frac{\hbar^2}{2m} \left(-\frac{L^3}{3} \right) \frac{30}{L^5} \\
&= \frac{5\hbar^2}{mL^2}
\end{aligned}$$

□

Problem 7

In Chapter VI we showed that an attractive square well has at least one bound state no matter how weak the potential. Use the Rayleigh-Ritz variational method to prove that this is a general property of *any* potential which is purely attractive. Do this by using the trial function

$$\psi = e^{-\alpha x^2}$$

and showing that α can always be chosen so that $E'(\alpha)$ is negative. (Why does this constitute a proof?)

Solution: The expectation value for any Hamiltonian using this trial wavefunction is:

$$\langle H \rangle = E(\alpha) = \int e^{-\alpha x^2}\left(\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)e^{-\alpha x^2}dx = \frac{\hbar^2}{2m}\sqrt{\frac{\alpha\pi}{2}} + \int_{-\infty}^{\infty} e^{-2\alpha x^2}V(x)dx$$

For any $V(x)$, we can choose the minimum point of $V(x)$ to equal zero, so that $V(x) > 0$ for all x. Now, we find $E'(\alpha)$:

$$\begin{aligned}
E'(\alpha) &= \frac{\hbar^2}{2m}\sqrt{\frac{\pi}{2}}\cdot\frac{1}{2\sqrt{\alpha}} + \frac{\partial}{\partial\alpha}\int_{-\infty}^{\infty} e^{-2\alpha x^2}V(x)dx \\
&= \frac{\hbar^2}{4m}\sqrt{\frac{\pi}{2\alpha}} + \int_{-\infty}^{\infty}\frac{\partial}{\partial\alpha}e^{-2\alpha x^2}V(x)dx \\
&= \frac{\hbar^2}{4m}\sqrt{\frac{\pi}{2\alpha}} - \int_{-\infty}^{\infty} 2x^2V(x)e^{-2\alpha x^2}dx
\end{aligned}$$

Now we ask what happens when we vary α. As α gets large, the first term becomes smaller, and at the same time, the second term becomes larger. This is because we can think of the $e^{-2\alpha x^2}$ term almost like a "weight" attached to $2x^2V(x)$, so by increasing the value of α we are increasing the weight of each term, thereby increasing the total value of the integral. Using this logic, we can imagine a point where we've increased α enough such that the second term is larger in magnitude than the first term, which causes $E'(\alpha)$ to become negative. This also works in general, since α can be as large as we want. □
