Chem 3502/4502 **Physical Chemistry II (Quantum Mechanics)** 3 Credits

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Solved Homework

We are given a perturbing potential $V = k\ (\ 1 - x\ )$ for a particle in an otherwise "normal" box of length 1. The first order correction to the ground-state energy is simply the expectation value of the perturbing operator for the exact eigenfunction that would exist in the *absence* of the perturbation. That is

$$a_1^{(1)} = \left\langle \Psi_1^{(0)}(x) \middle| k(1-x) \middle| \Psi_1^{(0)}(x) \right\rangle$$

where Ψ_1 is the ground state particle-in-a-box wave function

$$\Psi_1^{(0)}(x) = \sqrt{2}\sin(\pi x) \quad 0 \le x \le 1$$

$$E_1^{(0)} = \frac{\pi^2}{2} = a_1^{(0)}$$

(note that although our formal derivations used subscript "0" to represent a ground state, for the particle in a box the ground state quantum number is $n = 1$). The energy of the ground state in the absence of the perturbation is the zero-order eigenvalue plus the first order correction.

We may expand the expectation value above as

$$\begin{aligned} a_1^{(1)} &= k\left[\left\langle \Psi_1^{(0)}(x) \middle| \Psi_1^{(0)}(x) \right\rangle - \left\langle \Psi_1^{(0)}(x) \middle| x \middle| \Psi_1^{(0)}(x) \right\rangle\right] \\ &= k\left(1 - \frac{1}{2}\right) \\ &= \frac{k}{2} \end{aligned}$$

where in making the first set of simplifications we have made use of the normalization of the ground-state wave function (so the first integral is 1) and our prior knowledge that $\langle x \rangle$ for a particle in a box wave function is always $L/2$, which in this case is 1/2.

Note that the result is completely intuitive. It says that, to first order, the ground state energy goes up by $k/2$. This is the value that the perturbing function has in the middle of the box, and it is what we would obtain as an *exact* answer if the bottom of the box had potential $k/2$ instead of the usual convention of zero. Since the perturbing function is linear, if the wave function doesn't change from that of the ground state it will feel the influence of the left-hand side and right-hand side of the perturbation equally so that it will indeed be as though the whole wave function feels the average of the perturbation (or $k/2$).

Of course, the wave function *will* relax to decrease its amplitude in the region of higher potential and increase it in the region of lower potential. That is the next part of the problem. From perturbation theory, we know that the first-order change in the wave function will be

$$\Psi_1^{(1)} = \sum_{j>1} c_j \Psi_j^{(0)}$$

where the coefficients multiplying the exact excited-state wave functions in the sum on the r.h.s. are given by

$$c_j = \frac{\left\langle \Psi_j^{(0)} \middle| \mathbf{V} \middle| \Psi_0^{(0)} \right\rangle}{a_0^{(0)} - a_j^{(0)}}$$

If we evaluate the coefficient equation for a generic exact excited-state particle-in-a-box wave function we have

$$\begin{aligned}
c_j &= \frac{\left\langle \sqrt{2}\sin(j\pi x) \middle| k(1-x) \middle| \sqrt{2}\sin(\pi x) \right\rangle}{\dfrac{\pi^2}{2} - \dfrac{j^2\pi^2}{2}} \\
&= \frac{4k}{\pi^2}\left[\frac{\left\langle \sin(j\pi x) \middle| \sin(\pi x) \right\rangle - \left\langle \sin(j\pi x) \middle| x \middle| \sin(\pi x) \right\rangle}{1 - j^2}\right] \\
&= \frac{4k}{\pi^2\left(j^2-1\right)} \int_0^1 \sin(j\pi x)\, x \sin(\pi x)\, dx \\
&= \frac{4k}{\pi^2\left(j^2-1\right)} \int_0^1 x\left\{\cos\left[(j-1)\pi x\right] - \cos\left[(j+1)\pi x\right]\right\} dx
\end{aligned}$$

From an integral table, we may determine

$$\int_0^1 x\cos\left[(j\pm 1)\pi x\right]dx = \frac{x}{(j\pm 1)\pi}\sin\left[(j\pm 1)\pi x\right]\Bigg|_0^1$$
$$+\frac{1}{(j\pm 1)^2\pi^2}\cos\left[(j\pm 1)\pi x\right]\Bigg|_0^1$$
$$= 0 - 0 + \frac{(-1)^{j-1}}{(j\pm 1)^2\pi^2} - \frac{1}{(j\pm 1)^2\pi^2}$$
$$= \begin{cases} 0 & j \text{ odd} \\ -\dfrac{2}{(j\pm 1)^2\pi^2} & j \text{ even} \end{cases}$$

Prior to plugging this result back in to the coefficient equation, let us ponder the implications that only excited states with even j contribute to the perturbed ground-state wave function. The reason is that these wave functions have odd parity about the center of the box. Thus, they can be added to the ground state in a way that decreases the wave function to the left and increases it to the right (where the potential is lower). Wave functions with odd j have even parity about the box midpoint, so any sum of one of these wave functions with the ground state will be unable to shift amplitude from one side to another!

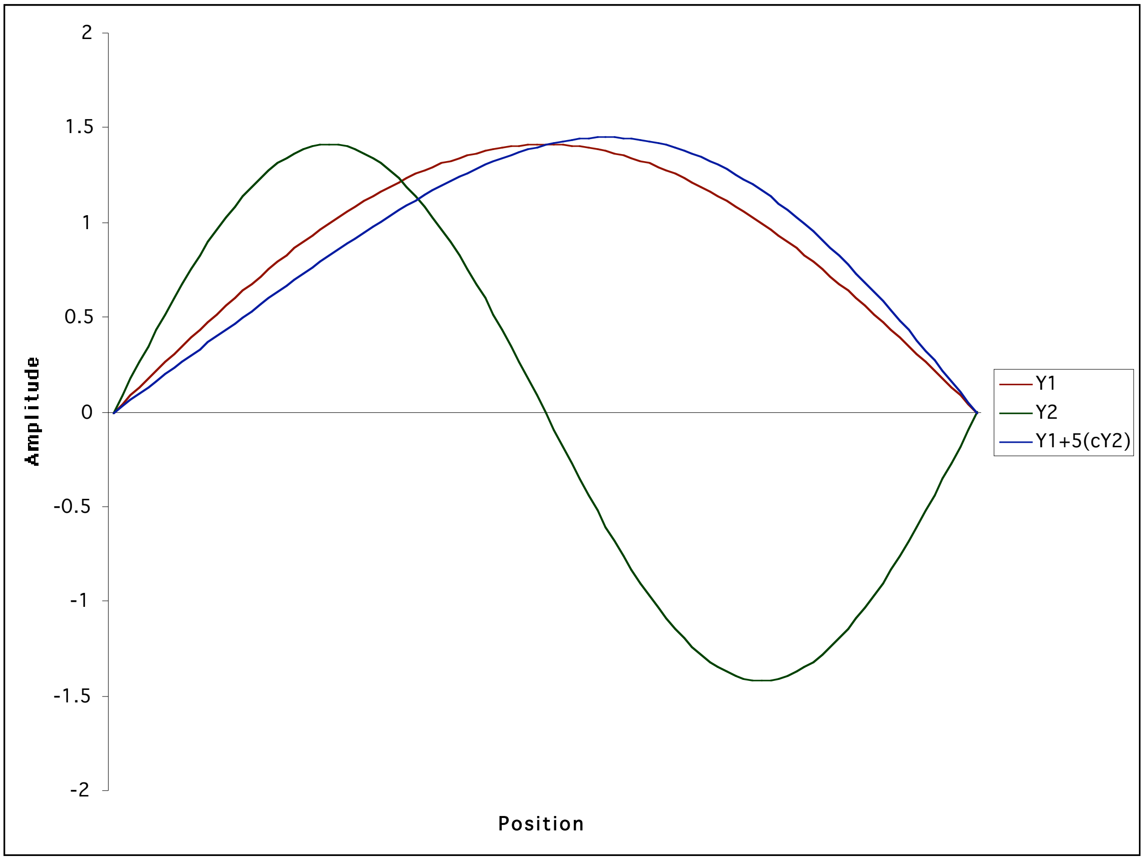
Alright, let's finally put it all together

$$c_j = \frac{4k}{\pi^2\left(j^2-1\right)}\int_0^1 x\left\{\cos\left[(j-1)\pi x\right] - \cos\left[(j+1)\pi x\right]\right\}dx$$
$$= \frac{4k}{\pi^2\left(j^2-1\right)}\left[-\frac{2}{(j-1)^2\pi^2} + \frac{2}{(j+1)^2\pi^2}\right]$$
$$= \frac{4k}{\pi^2(j+1)(j-1)}\left[\frac{2(j-1)^2 - 2(j+1)^2}{(j+1)^2(j-1)^2\pi^2}\right]$$
$$= -\frac{32j}{\pi^4(j+1)^3(j-1)^3}k \quad j \text{ even}$$

So, the coefficients increase with increasing k, which makes sense, since increasing k means an increasing perturbation. Also, if $k = 0$ there is no perturbation and all coefficients are zero meaning that there is no change to the ground-state wave function. Both these points represent a sanity check on our result.

Note also that the coefficients become small rather quickly owing to the j^{-5} scaling of our coefficient expansion. If we consider the dominant contribution from the first excited state, $j = 2$, it is evidently $-(64/27\pi^4)k$, or about $-0.0243k$. Higher states make almost negligible contributions, so the net change in the ground-state wave function is really rather small. The reason the wave function resists shifting to the left more strongly is that such a shift increases the curvature in the right side of the box, and hence the kinetic energy goes up.

Shown below is the graphical depiction of what we have done above for the case $k = 5$. The unperturbed ground-state wave function is shown in red, the unperturbed first excited-state wave function in green, and the perturbed ground-state wave function in blue.



Review and Catch-up

I'll try to give a recapitulation of key points to be covered by Exam III, but I am particularly eager to field questions from the class. Please be prepared to ask about any issues that you have found confusing or unclear!

Homework (n/a, study for Exam III)

Example Problems

1. If Φ is a guess wave function, H is the Hamiltonian, and E_0 is the ground-state energy, which of the following is/are *always* true as a consequence of the variational principle?

(a) $\int \Phi^* H \Phi d\mathbf{r} \geq E_0$

(b) $\langle \Phi | H | \Phi \rangle \geq E_0 \langle \Phi | \Phi \rangle$

(c) The expectation value of H over Φ will be less than E_0

(d) The expectation value of H over Φ will be greater than E_0 + 1/2 a.u.

(e) $\dfrac{\int \Phi^* H \Phi d\mathbf{r}}{\int \Phi^* \Phi d\mathbf{r}} > E_0$

(f) (a) and (b)

(g) (a) and (e)

(h) (a), (b), and (e)

2. What is < 1/r > in a.u. for the one-electron wave function $\psi_{1s}(r,\theta,\phi;\alpha) = e^{-\alpha r}$?

(a) 0

(b) 1/2

(c) 1

(d) π / α

(e) $4\pi / (2\alpha)^2$

(f) α

(g) 2α

(h) None of the above

(A useful formula: $\int_0^\infty xe^{-ax}dx = \dfrac{1}{a^2}$)

3. Which of the below statements is/are true?

(a) Fermions have integer spin

(b) Fermion wave functions must be symmetric

(c) Bosons have half-integer spin

(d) Boson wave functions can be symmetric or antisymmetric

(e) $\Psi = a(1)b(2) - b(1)a(2)$ is a valid fermion wave function

(f) Boson wave functions vanish when two particles have identical one-particle wave functions

(g) (a), (b), (c), and (e)

(h) All of the above

4. For a three-electron wave function Ψ, $\langle \Psi | S^2 | \Psi \rangle = 0.75$. Which of the below statements about Ψ is/are true?

(a) The quantum number $S = 1/2$

(b) Ψ is not a pure spin state

(c) Ψ cannot be normalized

(d) Ψ cannot be antisymmetric

(e) Ψ is a doublet state

(f) (a) and (e)

(g) (c) and (d)

(h) All of the above