

Supplementary subject: Quantum Chemistry

Problem set for the lectures in perturbation theory

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1. We normally think of the one-dimensional well as being horizontal. Suppose it is vertical; then the potential energy of the particle depends on x because of the presence of the gravitational field. Calculate the first order correction to the zero-point energy, and evaluate it for an electron in a box on the surface of the Earth. Account for the result. *Hint:* The energy of the particle depends on its height as mgx where $g = 9.81ms^{-2}$. Because g is so small, the energy correction is tiny; but it would be significant if the box were on the surface of a neutron star.
2. Calculate the second order correction to the energy for the system described in the previous problem and calculate the first order ground state wavefunction. Account for the shape of the distortion caused by the perturbation. *Hint:* You will encounter the integral

$$\int x \sin ax \sin bx dx = -\frac{d}{da} \int \cos ax \sin bx dx$$

$$\int \cos ax \sin bx dx = \frac{\cos(a-b)x}{2(a-b)} - \frac{\cos(a+b)x}{2(a+b)} .$$

Evaluate the sum over n numerically.

3. Repeat the previous problem, but estimate the second order energy correction using the closure approximation. Compare the two calculations and deduce the appropriate value of ΔE .
4. Following an approach similar to that employed to obtain the expression for $|n^{(1)}\rangle$ in non-degenerate time-independent perturbation theory, derive the following expression for the second order correction to the wavefunction (assume that the expression for $|n^{(1)}\rangle$ is known):

$$|n^{(2)}\rangle = \sum_{k \neq n} |k^{(0)}\rangle \left[\frac{\langle k^{(0)} | \hat{H}^{(2)} | n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}} + \sum_{l \neq n} \frac{\langle k^{(0)} | \hat{H}^{(1)} | l^{(0)} \rangle \langle l^{(0)} | \hat{H}^{(1)} | n^{(0)} \rangle}{(E_n^{(0)} - E_k^{(0)})(E_n^{(0)} - E_l^{(0)})} - \frac{\langle k^{(0)} | \hat{H}^{(1)} | n^{(0)} \rangle \langle n^{(0)} | \hat{H}^{(1)} | n^{(0)} \rangle}{(E_n^{(0)} - E_k^{(0)})^2} \right] .$$

5. Assume that $\hat{H}^{(0)}$ is the Hamiltonian of a one-dimensional harmonic oscillator centred at $x = 0$ and that there is a perturbation $\hat{H}^{(1)} = \gamma \hat{x}$ where γ is a real constant. Calculate the first and second order corrections to the energy. Then, by observing that actually $\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}$ also happens to be the Hamiltonian of a slightly modified (say how) harmonic oscillator, show that the energy you have calculated up to the second order is exact for \hat{H} .

6. In time-independent degenerate perturbation theory assume that we can find a Hermitian operator \hat{A} which commutes with both $\hat{H}^{(0)}$ and $\hat{H}^{(1)}$. Also assume that the \hat{A} eigenvalues of the common eigenfunctions of $\hat{H}^{(0)}$ and \hat{A} are all different from each other. Show that these common eigenfunctions are the “correct” ones for the perturbation $\hat{H}^{(1)}$.
7. Use the formalism of perturbation theory for a time-dependent perturbation and the expression for the first order expansion coefficient for the time-dependent wavefunction, $a_f^{(1)}(t) = \frac{1}{i\hbar} \int_0^t H_{fj}^{(1)}(t') e^{i\omega_{fj}t'} dt'$ to derive the second order expansion coefficient:

$$a_f^{(2)}(t) = \left(\frac{1}{i\hbar}\right)^2 \sum_k \int_0^t dt' \int_0^{t'} dt'' e^{i\omega_{fk}t'} H_{fk}^{(1)}(t') e^{i\omega_{kj}t''} H_{kj}^{(1)}(t'') .$$

8. Calculate the probability of finding a system in the state $|f^{(0)}\rangle$ if initially it was in the state $|j^{(0)}\rangle$ and a constant perturbation was applied at $t = 0$.
9. A hydrogen atom in a $2s^1$ configuration passes into a region where it experiences an electric field in the z -direction for a time τ . What is its electric dipole moment during its exposure and after it emerges? [The dipole moment is the expectation value of $e\hat{z}$. The integral $\int \psi_{2s}\hat{z}\psi_{2p_z} d\mathbf{r}$ is equal to $3a_0$.]
10. An electric field, \mathcal{E} , in the z -direction is increased linearly with time, starting from zero. What is the probability that a hydrogen atom, initially in the ground state, will be found with its electron in a $2p_z$ orbital at time t ?
11. At $t = T/2$ the strength of the field used in the previous problem begins to decrease linearly. What is the probability that the electron is in the $2p_z$ orbital at $t = T$? What would the probability be if initially the electron was in a $2s$ orbital?
12. Assume in the previous problem that the perturbation instead of being switched linearly it was switched on and off exponentially and slowly, the switching off commencing long after the switching on was complete. Calculate the probabilities, long after the perturbation has been extinguished, of the $2p_z$ orbital being occupied, the initial state being the $1s$. *Hint:* Take $\hat{H}^{(1)} \propto (1 - e^{-kt})$ for $0 \leq t \leq T$ and $\hat{H}^{(1)} \propto e^{-k(t-T)}$ for $t \geq T$. Interpret “slow” as $k \ll \omega$ and “long after” as $k(t - T) \gg 1$ (for “long after switching off”).
13. Examine how the A and B coefficients depend on the length of a one-dimensional square well for the transition $n + 1 \rightarrow n$. *Hint:* You will need the integral:

$$\int x \sin ax \sin bx dx = \frac{x \sin(a-b)x}{2(a-b)} - \frac{x \sin(a+b)x}{2(a+b)} + \frac{\cos(a-b)x}{2(a-b)^2} - \frac{\cos(a+b)x}{2(a+b)^2}$$

14. Model an atom by an electron in a one-dimensional box of length L . (Assume there to be an “invisible” positive charge at the centre of the box which provides the positive end of the dipole but does not affect the wavefunctions.) Calculate the polarizability of the system parallel to its length. *Hint:* The procedure and results of Problem 2 can be used.
15. Establish a perturbation theory expression for the components of the first hyperpolarizability β_{zzz} of a non-polar molecule. *Hint:* You will need to use the following expression for the third order correction to the energy

$$E_0^{(3)} = \sum_{m \neq 0} \sum_{n \neq 0} \frac{H_{0m}^{(1)} H_{mn}^{(1)} H_{n0}^{(1)}}{(E_m^{(0)} - E_0^{(0)})(E_n^{(0)} - E_0^{(0)})} - H_{00}^{(1)} \sum_{k \neq 0} \frac{H_{0k}^{(1)} H_{k0}^{(1)}}{(E_k^{(0)} - E_0^{(0)})^2} .$$

16. Use the closure approximation to estimate the polarizability of a hydrogen atom in its ground state. *Hint:* The main work of the calculation is the evaluation of $\langle r^2 \rangle$; use the following expressions for the ground state wavefunction and the energy levels of the atom

$$\psi_{1s}(\mathbf{r}) = \left(\frac{Z^3}{\pi a_0^3} \right)^{\frac{1}{2}} e^{-Zr/a_0} , \quad E_n = -\frac{Z^2 \mu e^4}{2\hbar^2 n^2}$$

and take the average energy difference for the closure approximation to be equal to the ionization energy of the hydrogen atom from its ground state.

17. Consider two particles, each in a one-dimensional box, with the centres of the boxes separated by a distance R . Each system may be regarded as a model of an atom in the same sense as in Problem 14. Calculate the dispersion energy (using the full second order energy expression and not the closure approximation) when the boxes are (a) in line, (b) broadside on. *Hint:* Note that the dipole moment operators have only one component in a one-dimensional system and that much of the calculational work has been done in Problem 14.
18. Use Møller-Plesset perturbation theory to obtain an expression for the ground state wavefunction corrected to first order in the perturbation.