Part II: Michaelmas 2021

Advanced Quantum Mechanics Question Sheet III

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Question 1. Perturbation theory in rotational dynamics

Suppose that a rigid diatomic molecule, having moment of inertia I and permanent dipole moment $\mathbf{d}$, is constrained to rotate in the $x-y$ plane.

By considering $\hat{L}_z$, show that the Hamiltonian is given by

$$\hat{H}_0 = -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2}. \tag{1}$$

Derive the three lowest-order energy eigenvalues of the freely rotating system, and their corresponding wavefunctions.

A weak, static electric field $\mathbf{E}$ is applied in the direction of the y axis. Find the matrix elements of the associated perturbation in the basis of the energy states of the freely rotating system. Present your results in terms of $|\mathbf{d}|$, I and $|\mathbf{E}|$.

Calculate to second order the new energies of the three lowest-energy states.

Are there any degeneracies, and does the perturbation split them?

Question 2. Perturbation theory of an electron trap

Consider an electron that is (i) constrained to move in 1D, and (ii) subject to periodic boundary conditions at $x = -L/2$ and $x = +L/2$. An electron trap is introduced in the form of a small potential well having the form

$$-V_0 e^{-x^2/a^2}, \tag{2}$$

where $a < L$.

Explain why, in the absence of the perturbation, the system has degenerate states.

Show that the perturbed energy eigenvalues of degenerate pairs take the form

$$E_{n,\pm} = E_n^0 - \sqrt{\pi} V_0 \frac{a}{L}\left(1 \pm e^{-k_n^2 a^2}\right) : \tag{3}$$

Draw a graph to illustrate the way in which degeneracy returns as ka is increased from 0 to 2π.

Explain, without proof, how the effect of introducing the perturbation differs between the cases where (i) the unperturbed potential has periodic boundary conditions at $x = -L/2$ and $x = +L/2$, and (ii) hard boundary conditions where the potential tends to $+\infty$ at $x = -L/2$ and $x = +L/2$.

Question 3. Perturbation Theory of the hydrogen nucleus

The energy levels of the hydrogen atom are influenced by the finite size of the proton. A simple model of this effect is to treat the proton as a uniformly charged hollow spherical shell of radius $b = 5 \times 10^{-16}$ m.

Show that, for this model, the change in the electrostatic potential energy corresponds to introducing a perturbation

$$H^1 = \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r} - \frac{1}{b}\right) \qquad r < b \tag{4}$$

into the normal Schrödinger equation for the hydrogen atom.

Using first-order perturbation theory, estimate the energy shifts of the hydrogen 2s and 2p states, and comment on your findings.

Why is the energy shift the same for all three 2p states, and why can each of the 2s and 2p states be considered independently even though they are initially degenerate?

[Hint: The integrals can be simplified considerably by noting that the size of the nucleus is much smaller than the atomic Bohr radius, i.e. $b \ll a_0$.

The 2s and 2p hydrogen atom wavefunctions are

$$\psi_{2s} = \sqrt{\frac{1}{8\pi a_0^3}}\left(1 - \frac{r}{2a_0}\right)e^{-r/2a_0}, \quad \psi_{2\mathrm{p}_0} = \frac{re^{-r/2a_0}}{\sqrt{32\pi a_0^5}}\cos\theta, \quad \psi_{2\mathrm{p}_{\pm 1}} = \mp\frac{re^{-r/2a_0}}{\sqrt{64\pi a_0^5}}e^{\pm i\phi}\sin\theta.] \tag{5}$$

Question 4. Perturbation Theory and the polarizability of hydrogen

An applied electric field $\boldsymbol{E}$ can induce a dipole moment in an atom according to the expression $\alpha\epsilon_0\boldsymbol{E}$ where α is the polarisibility.

The polarisibility of the hydrogen atom in its ground state may be estimated using perturbation theory.

Working to second order in the electric field strength, show that the energy shift in the ground state $|0\rangle$ is

$$\Delta E = (eE)^2 \sum_{k\neq 0} \frac{|\langle k|z|0\rangle|^2}{E_0 - E_k}\,, \tag{6}$$

where E_k is the unperturbed energy of state $|k\rangle$. Hence show that the polarisability is

$$\alpha = \frac{2e^2}{\epsilon_0} \sum_{k\neq 0} \frac{|\langle k|z|0\rangle|^2}{E_k - E_0}\,. \tag{7}$$

Show that the same result may be obtained from the perturbed wavefunction to first-order in $\boldsymbol{E}$ by evaluating the expectation value of the induced electric dipole moment.

Evaluation of α is tedious, but a useful upper bound may be obtained by noting that $E_k \geq E_1$, where E_1 is the energy of the first excited state. Using this observation, show that $\alpha \leq (64/3)\pi a_0^3$. Compare this upper bound with the experimental value of $\alpha = 8.5 \times 10^{-30}\,\mathrm{m}^3$.

$\Big[$ The ground state of the hydrogen atom, $|0\rangle \equiv (\pi a_0^3)^{-1/2} e^{-r/a_0}$, will be needed to compute the matrix element $\langle 0|z^2|0\rangle$. $\Big]$

Question 5. Degenerate perturbation theory of 2D simple harmonic motion

A particle of mass m is constrained to move in the xy–plane such that the Hamiltonian is given by

$$\hat{H} = \frac{1}{2m}(\hat{p}_x^2 + \hat{p}_y^2) + \frac{1}{2}m\omega^2(\hat{x}^2 + \hat{y}^2) + \lambda\hat{x}\hat{y}\,.$$

(a) Using raising and lowering operators show that for $\lambda = 0$ the (unperturbed) energy eigenvalues can be described by the equation $E_{n_x,n_y} = (n_x + n_y + 1)\hbar\omega$.

(b) For the ground state and first two excited states, describe the unperturbed eigenstates for the system in terms of one-dimensional harmonic oscillator eigenstates $|n_x\rangle$, $|n_y\rangle$. What are the degeneracies of each of these energy levels ?

(c) For the case $\lambda \neq 0$, use degenerate perturbation theory to determine the energy splitting for the lowest energy degenerate level, as well as the first-order corrections to the wavefunctions.

Question 6. Variational analysis of 1D simple harmonic motion

Use a trial wavefunction of the form

$$\psi(x) = \begin{cases} A(a^2 - x^2) & -a < x < a \\ 0 & \text{otherwise} \end{cases} \tag{8}$$

to place an upper bound on the ground state energy of a one-dimensional harmonic oscillator having the potential $V(x) = m\omega^2 x^2/2$, where m is the mass of the particle and ω the natural frequency.

Compare your answer with the exact result, and comment. Why is the result slightly different to the actual ground-state energy?

Question 7. Variational analysis

Use variational techniques to answer the following:

(a) E_1 and E_2 are the ground state energies of a particle moving in attractive potentials $V_1(\boldsymbol{r})$ and $V_2(\boldsymbol{r})$, respectively. Using the variational method, show that $E_1 \leq E_2$ if $V_1(\boldsymbol{r}) \leq V_2(\boldsymbol{r})$.

[Hint: Use the wavefunction of a particle moving in $V_2(\boldsymbol{r})$ as a trial wavefunction for the potential $V_1(\boldsymbol{r})$.]

(b) Consider a particle moving in a localized one-dimensional attractive potential $V(x)$, i.e. a potential such that $V(x) \leq 0$ for all x, and $V(x) \to 0$ as $|x| \to \infty$. Use the variational principle with trial function $A\exp(-\lambda x^2)$ to show that the upper bound on the ground state energy is negative, and hence that for any such potential at least one bound state must exist.

Question 8. Time-dependent perturbation theory

As shown in lectures, the probability that a system initially prepared in energy eigenstate ψ_0 at time $t = 0$ is subsequently found in a state ψ_n when a weak perturbation $V(t)$ is applied is given approximately by $|c_n(t)|^2$ where

$$c_n(t) = \frac{1}{i\hbar} \int_0^t e^{i(E_n - E_0)t'/\hbar} \langle \psi_n | \hat{V}(t') | \psi_0 \rangle \, \mathrm{d}t' \, .$$

where the perturbation $\hat{V}(t')$ is in the Schrödinger picture.

(i) At times $t > 0$, an electric field $\mathcal{E}_z = \mathcal{E}_0 \exp(-t/\tau)$ is applied to a hydrogen atom, initially prepared in its ground state. Working to first order in the electric field, show that, after a long time, $t \gg \tau$, the probability of finding the atom in the 2s state is zero.

(ii) Likewise, show that the probability of finding the atom in the $2p_0$ state is given by

$$P(2p_0) = |c_{2p_0}(\infty)|^2 = \frac{e^2 \mathcal{E}_0^2 a_0^2 2^{15}}{3^{10}} \cdot \frac{1}{\Delta E^2 + \hbar^2/\tau^2} \, .$$

Question 9. Time-dependent perturbation theory of simple harmonic motion

A one-dimensional harmonic oscillator with Hamiltonian $\hat{H}_0 = (\hat{p}_x^2/2m) + \frac{1}{2}m\omega^2\hat{x}^2$, initially in the ground state, is subjected to the perturbation

$$\hat{H}'(t) = \begin{cases} 0 & t < 0 \text{ and } t > T \\ \lambda\hat{x}(1 - t/T) & 0 \leq t \leq T \end{cases} .$$

Find, to first order in λ, the probability that the oscillator is in the first excited state at time $t > T$.

Verify that for $\omega T \gg 1$ this probability approaches the value $|\langle\psi_1|\psi_0'\rangle|^2$ where $|\psi_0'\rangle$ is the ground state for the Hamiltonian $\hat{H}_0 + \lambda\hat{x}$.

[The ground and first excited states have the wavefunctions:

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \exp\left(-\frac{m\omega}{2\hbar}x^2\right), \qquad \psi_1(x) = \left(\frac{2m\omega}{\hbar}\right)^{1/2} x\psi_0(x) .$$

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