Quantum Mechanics: Worksheet 7

Fine structure: relativistic kinetic energy and Darwin term

Christophe De Beule (christophe.debeule@gmail.com)

---

1 Hellmann-Feynman theorem

Consider a Hamiltonian $H(\boldsymbol{\lambda})$ that depends on n parameters $\boldsymbol{\lambda}$. Prove that, for a *normalized* eigenstate $\psi(\boldsymbol{\lambda})$ of $H(\boldsymbol{\lambda})$, we have

$$\frac{\partial E}{\partial \lambda_i} = \langle \psi(\boldsymbol{\lambda}) | \frac{\partial H}{\partial \lambda_i} | \psi(\boldsymbol{\lambda}) \rangle, \qquad (i = 1, \ldots, n).$$

This is the Hellmann-Feynman theorem. Consider the harmonic oscillator and use this theorem to calculate $\langle n|x^2|n\rangle$ and $\langle n|p^2|n\rangle$. The Hamiltonian is

$$H(\omega, \hbar) = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2.$$

2 Relativistic correction to the kinetic energy

In non-relativistic mechanics, the kinetic energy is

$$\frac{\boldsymbol{p}^2}{2m}.$$

However, in relativistic mechanics, the kinetic energy becomes

$$\sqrt{\boldsymbol{p}^2 c^2 + m^2 c^4} - mc^2 = \frac{\boldsymbol{p}^2}{2m} - \frac{\boldsymbol{p}^4}{8m^3c^2} + \cdots,$$

so the first-order kinetic energy correction to the Hamiltonian is

$$H_{\text{kin}} = -\frac{\boldsymbol{p}^4}{8m^3c^2}.$$

In quantum mechanics, the first-order correction to the energy due to this perturbation becomes (in nondegenerate perturbation theory)

$$E_n^{(1)} = \langle n^{(0)} | H_{\text{kin}} | n^{(0)} \rangle = -\frac{1}{2mc^2} \langle n^{(0)} | \left(\frac{\boldsymbol{p}^2}{2m} \right)^2 | n^{(0)} \rangle.$$

(a) Consider the hydrogen-like atom $H_0 = \boldsymbol{p}^2/2m + V$, and rewrite the first-order correction in terms of the unperturbed energy and the expectation values of V and V^2, where V is the Coulomb potential.

(b) The Hamiltonian that appears in the radial part of the Schrödinger equation for the hydrogen-like atom, i.e. $H_r R_{nl}(r) = E_n R_{nl}(r)$, is given by

$$H_r(l, Z) = -\frac{\hbar^2}{2m_e r^2} \left[\frac{d}{dr} \left(r^2 \frac{d}{dr} \right) - l(l+1) \right] - \frac{Ze^2}{r}.$$

Calculate the expectation value of r^{-1} and r^{-2} with the Hellmann-Feynman theorem. Note that the principal quantum number is given by $n(l) = n_r + l + 1$, where n_r is the radial quantum number, i.e. the number of nodes of $R_{nl}(r)$.

(c) What is the degeneracy of the n-th level of the hydrogen-like atom? Why is the operator $\boldsymbol{p}^4$ already diagonal in the $|nlm\rangle$ basis?

(d) Find an expression for the first-order kinetic energy correction $E_{\text{kin}}^{(1)}$.

3 Darwin term

The Darwin term is given by

$$H_{\text{Darwin}} = \frac{\hbar^2}{8m^2c^2}\nabla^2 V.$$

(a) Use the definition of the electric field $\boldsymbol{\mathcal{E}}$ and Gauss's law to show that for the hydrogen-like atom (in Gaussian units)

$$H_{\text{Darwin}} = \frac{\hbar^2}{8m_e^2c^2}4\pi Ze^2\delta(\boldsymbol{r}).$$

The Darwin term changes the effective potential at the nucleus. It can be interpreted as a smeared out electrostatic interaction between the electron and the nucleus due to rapid quantum oscillations of the electron (Zitterbewegung).

(b) Is the Darwin term diagonal in each degenerate subspace? Find the first-order correction $E^{(1)}_{\text{Darwin}}$ to the energy of the hydrogen-like atom.

Hydrogen-like atom

The energy levels of the nonrelativistic hydrogen-like atom are (in Gaussian units)

$$E_n = -\frac{Z^2e^2}{2a_0n^2}, \qquad (n = 1, 2, \ldots)\,,$$

where $a_0 = \frac{\hbar^2}{m_e e^2}$ is the Bohr radius. The value of the wave function at the nucleus is

$$\psi_{nlm}(0) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{na_0}\right)^{\frac{3}{2}}\delta_{l0}.$$