M520 Non-Relativistic Quantum Mechanics — Ninnat Dangniam

Homework Assignment 7

DUE: Wednesday 18 October 2023 — 40 points

1. Spin-orbit coupling (10 points).

Suppose that the outermost electron of a hydrogen-like atom is governed by a Hamiltonian

$$\widehat{H} = \widehat{H}_0 + \widehat{H}_{\mathrm{SO}} = \frac{\widehat{\mathbf{p}}^2}{2\mu} + V(r) + \frac{2b}{\hbar^2}\widehat{\mathbf{L}} \cdot \widehat{\mathbf{S}},$$

where b is a constant and $\widehat{\mathbf{S}} = \hbar\widehat{\sigma}/2$. Find the eigenstates and eigen-energies of $\widehat{H}$ in terms of the eigenstates $\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)Y_l{}^m(\theta,\varphi)$ and energies E_n of $\widehat{H}_0 = \widehat{\mathbf{p}}^2/2\mu + V(r)$.

Note that your eigenstates now lie in the joint Hilbert space $\mathcal{H}_L \otimes \mathcal{H}_S$ of the orbital and spin degrees of freedom, spanned by

$$|n,l,m\rangle \otimes \left|\frac{1}{2}, m_s\right\rangle,$$

where $\langle \mathbf{r}|n,l,m\rangle = \psi_{nlm}(\mathbf{r})$ and $m_s = \pm 1/2$. If you want to work in the coordinates form, a general "wave function" would have two components. For instance,

$$\alpha\,|n,l,m\rangle \otimes \left|\frac{1}{2},\frac{1}{2}\right\rangle + \beta\,|n',l',m'\rangle \otimes \left|\frac{1}{2},-\frac{1}{2}\right\rangle \doteq \begin{pmatrix} \alpha\psi_{nlm} \\ \beta\psi_{n'l'm'} \end{pmatrix},$$

where $\alpha = \langle +|\phi\rangle$ and $\beta = \langle -|\phi\rangle$ are the amplitudes of some state $|\phi\rangle$ in $\mathcal{H}_S$.

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2. The projection theorem (15 points).

Let $\hat{\mathbf{J}}$ be an angular-momentum vector operator, and $\widehat{\mathbf{V}}$ an arbitrary vector operator.

(a) Express it in terms of $\hat{J}_z, \hat{J}_\pm$ and $\widehat{V}^q$, where $\widehat{V}^q$ are the spherical components of $\widehat{\mathbf{V}}$.

(b) Show that

$$\left\langle k'j'm' \right| \hat{\mathbf{J}} \cdot \widehat{\mathbf{V}} \left| kjm \right\rangle = c\, \delta_{j'j}\, \delta_{m'm} \langle k'j \left\| \widehat{\mathbf{V}} \right\| kj\rangle,$$

where k is a quantum number which, together with j and m, uniquely determine the basis state, and c is a constant independent of k, k' and $\widehat{\mathbf{V}}$.

(c) Show that

$$\left\langle k'jm' \right| \widehat{V}^q \left| kjm \right\rangle = \frac{\langle k'j'm' | \hat{\mathbf{J}} \cdot \widehat{\mathbf{V}} | kjm\rangle}{j(j+1)\hbar^2} \left\langle k'jm' \right| \hat{J}^q \left| kjm \right\rangle.$$

This result is known as the *projection theorem*. Give a geometric interpretation of this theorem. **Hint:** Think of $\hat{\mathbf{J}}$ and $\widehat{\mathbf{V}}$ as ordinary vectors.

(d) As an application of the projection theorem, consider putting an atom in a weak, uniform magnetic field $\mathbf{B} = B\mathbf{e}_z$. The spin and the angular parts of the electron's dipole moment couple to the magnetic field, resulting in the Hamiltonian

$$\widehat{H} = \widehat{H}' + \widehat{H}_B,$$

where

$$\widehat{H}_B \approx \frac{eB}{2\mu c}\left(\widehat{L}_z + 2\widehat{S}_z\right),$$

and $\widehat{H}'$ is $\widehat{H}_0$ plus other low-order relativistic effects. Compute the first order correction to the energy $E_B^{(1)}$ due to $\widehat{H}_B$ treated as a perturbation to $\widehat{H}'$. Do we need degenerate perturbation theory?

(The other relativistic effects in $\widehat{H}'$ are of the order α^4, where $\alpha = e^2/\hbar c \approx 1/137$ is the fine structure constant. So we cannot treat $\widehat{H}_B$ as a perturbation to $\widehat{H}'$ when the magnetic field is of the order $2m_e c\alpha^4/e\hbar = \mu_e \alpha^4$, where $\mu_e \approx 5.8 \times 10^{-5}\text{eV} \cdot \text{T}^{-1}$ is the *Bohr magneton*. This is about $1/(137)^4 \approx 3 \times 10^{-9}$ times the magnitude of the Earth's magnetic field.)

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3. The Stark effect (15 points).

Consider a hydrogen atom in the presence of a static electric potential $\phi(\mathbf{r})$ from a faraway source. Place the nucleas at the origin and assume that it is infinitely massive. The interaction energy of the atom with the extermal field can be Taylor expanded around the origin:

$$E_{\text{int}} = \underbrace{e\mathbf{r} \cdot \mathbf{E}(0)}_{\text{Dipole}} \underbrace{- \frac{e}{2}\sum_{jk} x_j x_k \left[\frac{\partial^2 \phi}{\partial x_j \partial x_k}\right]_{\mathbf{r}=0}}_{\text{Quadrupole}} + \mathcal{O}(r^3)$$

Ignore the spins, and let $|nlm\rangle$ be the stationary states of the hydrogen atom without an external field.

(a) Choose the electric field to be in the z direction so that $H_{\text{int}} = e\mathbf{r} \cdot \mathbf{E}(\mathbf{0}) = eE(0)\hat{z}$. Give the selection rules for the intrinsic dipole moment between all stationary states. What is the intrinsic dipole moment in the ground state?

(b) Give the selection rules for the intrinsic quadrupole moment between all stationary states. show that the ground state cannot have an intrinsic quadrupole moment.

For the rest of the problem assume the dipole interaction only.

(c) What is the first order correction $E_{n=1}^{(1)}$ to the ground state energy? Write down the correction $|\psi_{n=1}\rangle^{(1)}$ to the ground state and show that the atom has an induced dipole that is linearly proportional to the electric field $\mathbf{E}$.

(d) The energy shift due to the induced dipole only appears as a second-order effect. Compute the second-order correction $E_{n=1}^{(2)}$ to the ground state energy. Simplify the expression using

$$E_1 - E_m = -13.6 \text{ eV} \cdot \left(1 - \frac{1}{m^2}\right) \approx -13.6 \text{ eV},$$

for $m \neq 1$.

(e) In a classical medium, when the induced dipole $\mathbf{p}$ is linearly proportional to an external field,

$$\mathbf{p} = \alpha \mathbf{E},$$

the constant α being as the *polarizability*, the dipole interaction energy is

$$E_{\text{int}} = -\frac{\alpha \mathbf{E}^2}{2}.$$

Given the approximation in **(d)**, find α for the hydrogen's ground state.