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Question 5: Stark effect. Derive a correction of energy and wavefunction.

The unperturbed Hamiltonian of the hydrogen atom is:

$$H_0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r} \tag{1}$$

The eigenstates of H_0 are given by the hydrogen wavefunctions $\psi_{n\ell m}$, with energies:

$$E_n^{(0)} = -\frac{13.6\,\mathrm{eV}}{n^2} \tag{2}$$

An external uniform electric field $\vec{E} = E\hat{z}$ adds a perturbation:

$$H' = eEz = eEr\cos\theta \tag{3}$$

The first-order correction to the energy is:

$$E_n^{(1)} = \langle n\ell m|H'|n\ell m\rangle \tag{4}$$

For $n = 1$, $\ell = 0$: Since ψ_{100} is spherically symmetric, the integrand involves $\cos\theta$, which is odd over the sphere:

$$E_1^{(1)} = eE\,\langle 100|z|100\rangle = 0 \tag{5}$$

We have two orbitals 2s and 2d.
If we ignore the states associated with spin, then
the total number of states to consider is four.
It means that we need to calculate the correction
of energy for each state (total number of corrections is 4!!! not 2)

So, no linear Stark effect for the ground state.

The $n = 2$ level has 4 degenerate states: $\psi_{200}, \psi_{210}, \psi_{211}, \psi_{21-1}$. Since the perturbation can mix these, we must diagonalize H' in this subspace.

The matrix elements of $H' = eEz$ are computed between these 4 states. Only the matrix elements between ψ_{200} and ψ_{210} are non-zero:

$$\langle 200|H'|210\rangle = \langle 210|H'|200\rangle = -3ea_0E \tag{6}$$

where a_0 is the Bohr radius.

The secular equation is of order 4, not 2.

So, in the basis $\{\psi_{200}, \psi_{210}\}$, the perturbation matrix is:

$$H' = \begin{pmatrix} 0 & -3ea_0E \\ -3ea_0E & 0 \end{pmatrix}$$

The eigenvalues of this matrix give the first-order energy corrections:

$$E^{(1)} = \pm 3ea_0E$$

So the energy levels split linearly with E: this is the linear Stark effect.

For non-degenerate states, the first-order correction to the wavefunction is:

$$\left|n^{(1)}\right\rangle = \sum_{k\neq n} \frac{\langle k|H'|n\rangle}{E_n^{(0)} - E_k^{(0)}}\,|k\rangle \tag{7}$$

For ψ_{100}, the dominant contribution comes from ψ_{210}:

$$|1s\rangle^{(1)} \approx \frac{\langle 210|eEz|100\rangle}{E_1^{(0)} - E_2^{(0)}}\,|210\rangle$$

Question 7:

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Stationary Case

Equation (a) is the time-independent Schrödinger equation with eigenstates φ_n^0 and energies E_n^0. The solution to the time-dependent Schrödinger equation (b) in the absence of perturbation is:

$$\psi_n^0(t) = \varphi_n^0 \, e^{-iE_n^0 t/\hbar} \tag{8}$$

This shows that the time evolution of a stationary state is simply a phase factor multiplying the spatial part φ_n^0.

Relation Between φ_n^0 and ψ_n^0

From the equation above, we see:

$$\psi_n^0(t) = \varphi_n^0 \, e^{-iE_n^0 t/\hbar}$$

So, φ_n^0 is the time-independent spatial part, and $\psi_n^0(t)$ is the full time-dependent wavefunction.

Time-Dependent Perturbation

When a time-dependent perturbation $\hat{H}'(t)$ is added, the total Hamiltonian becomes:

$$\hat{H}(t) = \hat{H}_0 + \hat{H}'(t)$$

and the full Schrödinger equation becomes:

$$i\hbar \frac{d}{dt}\psi_n(t) = \left(\hat{H}_0 + \hat{H}'(t)\right)\psi_n(t)$$

To solve this, we express the wavefunction as a linear combination of the unperturbed eigenstates:

$$\psi(t) = \sum_n c_n(t)\, \varphi_n^0 \, e^{-iE_n^0 t/\hbar} \tag{9}$$

Here, $c_n(t)$ are time-dependent coefficients that encode transitions between states due to the perturbation $\hat{H}'(t)$.

Question 13: What is the meaning of the theorem on the relationship between spin and statistics?

The Statement of the Theorem

- Particles with integer spin ($s = 0, 1, 2, \ldots$) are called bosons and obey Bose-Einstein statistics.
- Particles with half-integer spin ($s = \frac{1}{2}, \frac{3}{2}, \ldots$) are called fermions and obey Fermi-Dirac statistics.

Implications

- Fermions satisfy the Pauli exclusion principle: no two identical fermions can occupy the same quantum state. This principle explains the structure of the periodic table and the stability of matter.
- Bosons, on the other hand, can occupy the same quantum state, which leads to phenomena such as Bose-Einstein condensation and the operation of lasers.

Origin of the Theorem

The theorem is not derivable from non-relativistic quantum mechanics. It is a consequence of:

- **Lorentz invariance** (special relativity),
- **Locality** (no instantaneous action at a distance),
- **Positive energy** (the ground state energy is bounded from below).

In relativistic quantum field theory, the symmetry properties of the wavefunction under exchange of identical particles are directly related to their spin:

- Fermions: antisymmetric wavefunction under exchange.
- Bosons: symmetric wavefunction under exchange.

Summary Table

Spin	**Type**	**Statistics**	**Behavior**
$0, 1, 2, \ldots$	Bosons	Bose-Einstein	Can occupy same state
$\frac{1}{2}, \frac{3}{2}, \ldots$	Fermions	Fermi-Dirac	Obey Pauli exclusion