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1.1 Linear Equations for First-Order Corrections

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In degenerate perturbation theory, we start with an unperturbed Hamiltonian $\hat{H}_0$ that has degenerate energy levels. Let's consider the n-th energy level $E_n^{(0)}$ with degeneracy g_n, having orthonormal basis states $\{\left|\psi_n^{(0),i}\right\rangle\}_{i=1}^{g_n}$.

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The perturbed Hamiltonian is:

$$\hat{H} = \hat{H}_0 + \lambda \hat{V} \tag{1}$$

where $\hat{V}$ is the perturbation and λ is a small parameter.

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The zeroth-order wave function correction is expressed as:

$$\left|\psi_n^{(0)}\right\rangle = \sum_{i=1}^{g_n} c_i^{(0)} \left|\psi_n^{(0),i}\right\rangle \tag{2}$$

To find the first-order energy corrections $E_n^{(1)}$ and the coefficients $c_i^{(0)}$, we solve the eigenvalue problem within the degenerate subspace:

$$\sum_{j=1}^{g_n} \left\langle\psi_n^{(0),i}\right| \hat{V} \left|\psi_n^{(0),j}\right\rangle c_j^{(0)} = E_n^{(1)} c_i^{(0)} \tag{3}$$

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This gives us the system of linear equations:

$$\sum_{j=1}^{g_n} V_{ij} c_j^{(0)} = E_n^{(1)} c_i^{(0)}, \quad i = 1, 2, \ldots, g_n \tag{4}$$

where $V_{ij} = \left\langle \psi_n^{(0),i} \middle| \hat{V} \middle| \psi_n^{(0),j} \right\rangle$ are the matrix elements of the perturbation.

1.2 Secular Equation

The secular equation is obtained by requiring non-trivial solutions to the homogeneous system:

$$\sum_{j=1}^{g_n} (V_{ij} - E_n^{(1)} \delta_{ij}) c_j^{(0)} = 0 \tag{5}$$

This leads to the secular determinant:

$$\det\left(\mathbf{V} - E_n^{(1)} \mathbf{I}\right) = 0 \tag{6}$$

In matrix form:

$$\begin{vmatrix} V_{11} - E_n^{(1)} & V_{12} & \cdots & V_{1g_n} \\ V_{21} & V_{22} - E_n^{(1)} & \cdots & V_{2g_n} \\ \vdots & \vdots & \ddots & \vdots \\ V_{g_n 1} & V_{g_n 2} & \cdots & V_{g_n g_n} - E_n^{(1)} \end{vmatrix} = 0 \tag{7}$$

The roots of this secular equation give the first-order energy corrections $E_n^{(1)}$, and the corresponding eigenvectors provide the coefficients $c_i^{(0)}$ for the zeroth-order wave function corrections.

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2.1 Einstein's Theory of Radiation

Einstein's theory of radiation describes the interaction between atoms and electromagnetic radiation through three fundamental processes:

2.1.1 Induced Absorption

When an atom in a lower energy state $|i\rangle$ absorbs a photon and transitions to a higher energy state $|f\rangle$:

$$\text{Rate of absorption} = B_{if}\rho(\omega_{fi})N_i \tag{8}$$

where:

- B_{if} is the Einstein coefficient for induced absorption
- $\rho(\omega_{fi})$ is the energy density of radiation at frequency $\omega_{fi} = (E_f - E_i)/\hbar$
- N_i is the population of the initial state

2.1.2 Induced Emission (Stimulated Emission)

When an atom in a higher energy state $|f\rangle$ is stimulated by radiation to emit a photon and transition to a lower energy state $|i\rangle$:

$$\text{Rate of stimulated emission} = B_{fi}\rho(\omega_{fi})N_f \tag{9}$$

where B_{fi} is the Einstein coefficient for induced emission.

2.1.3 Spontaneous Emission

An atom in an excited state can spontaneously emit a photon and decay to a lower energy state:

$$\text{Rate of spontaneous emission} = A_{fi}N_f \tag{10}$$

where A_{fi} is the Einstein coefficient for spontaneous emission.

2.2 Reason for Spontaneous Transitions

Spontaneous transitions arise from the quantum mechanical nature of the electromagnetic field. Even in the absence of external radiation, quantum field theory shows that the electromagnetic field has zero-point fluctuations (vacuum fluctuations). These vacuum fluctuations provide the mechanism for spontaneous emission, as the atom can couple to these virtual photons in the vacuum state.

The spontaneous emission rate is given by:

$$A_{fi} = \frac{\omega_{fi}^3}{3\pi\epsilon_0\hbar c^3}|\langle f|\hat{\mathbf{d}}|i\rangle|^2 \tag{11}$$

where $\hat{\mathbf{d}}$ is the electric dipole moment operator.

2.3 Energy Emission vs. Absorption

Spontaneous transitions are related to *energy emission only*. In spontaneous emission, an excited atom loses energy by emitting a photon and transitioning to a lower energy state. There is no spontaneous absorption process because it would violate energy conservation (an atom cannot spontaneously gain energy from the vacuum).

2.4 Relation Between Spontaneous and Induced Transitions

The Einstein coefficients are related through detailed balance and thermodynamic equilibrium considerations:

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$$B_{if} = B_{fi} \tag{12}$$

$$A_{fi} = \frac{\hbar\omega_{fi}^3}{\pi^2 c^3} B_{fi} \tag{13}$$

The transition probabilities are:

$$P_{\text{absorption}} = B_{if}\rho(\omega_{fi})\Delta t \tag{14}$$

$$P_{\text{stimulated emission}} = B_{fi}\rho(\omega_{fi})\Delta t \tag{15}$$

$$P_{\text{spontaneous emission}} = A_{fi}\Delta t \tag{16}$$

The ratio of spontaneous to stimulated emission rates is:

$$\frac{A_{fi}}{B_{fi}\rho(\omega_{fi})} = \frac{\hbar\omega_{fi}^3}{\pi^2 c^3 \rho(\omega_{fi})} \tag{17}$$

This ratio increases with frequency cubed, explaining why spontaneous emission dominates at high frequencies (optical transitions), while stimulated processes dominate at low frequencies (radio transitions).

3 15.

3.1 Classical Schrödinger Equation

The time-dependent Schrödinger equation is:

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \hat{H}\Psi(\mathbf{r},t) \tag{18}$$

For a free particle, the Hamiltonian is:

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2 \tag{19}$$

Key characteristics:

- First-order in time derivative
- Second-order in spatial derivatives
- Non-relativistic (valid for $v \ll c$)
- Single-component wave function
- Describes spin-0 particles naturally

3.2 Dirac Equation

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The Dirac equation is:

$$(i\gamma^\mu \partial_\mu - mc/\hbar)\Psi = 0 \tag{20}$$

or in explicit form:

$$i\hbar \frac{\partial \Psi}{\partial t} = (c\boldsymbol{\alpha} \cdot \hat{\mathbf{p}} + \beta mc^2)\Psi \tag{21}$$

where $\boldsymbol{\alpha}$ and β are 4×4 Dirac matrices, and Ψ is a four-component spinor.

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Key characteristics:

- First-order in both time and spatial derivatives
- Fully relativistic
- Four-component wave function (spinor)
- Naturally incorporates spin-1/2
- Predicts antiparticles
- Reduces to Schrödinger equation in non-relativistic limit

3.3 Main Differences

1. **Relativistic vs. Non-relativistic**: Dirac equation is fully relativistic, while Schrödinger is non-relativistic
2. **Spin**: Dirac naturally incorporates spin-1/2, Schrödinger requires ad-hoc addition of spin
3. **Wave function components**: Schrödinger uses single-component wave functions, Dirac uses four-component spinors
4. **Antiparticles**: Dirac predicts existence of antiparticles, Schrödinger does not
5. **Energy spectrum**: Dirac allows negative energy solutions, leading to the concept of the Dirac sea
6. **Mathematical structure**: Dirac is first-order differential equation, Schrödinger is second-order in space

The Dirac equation reduces to the Schrödinger equation in the non-relativistic limit when particle velocities are much smaller than the speed of light.