PC3130

Quantum Mechanics II

Time-Independent Perturbation Theory
Application – Fine Structure of the Hydrogen Atom

Dirac Hamiltonian: Existence of Spin

The Pauli Hamiltonian contains the interaction of spin with an external magnetic field. For a particle in an external potential, or interacting with other particles, a spin-dependence can also be present via the exchange term. But the spin up and spin down Hamiltonians can be separated and solved independently.

$$
\begin{aligned}
H &= \boxed{H_{Pauli}} \\
&- \frac{p^4}{8m^3c^2} \qquad \text{mass} - \text{velocity} \\
&+ \frac{\hbar^2 q}{8m^2c^2}\nabla\cdot\nabla\phi(\mathbf{r}) \qquad \text{Darwin} \\
&- \frac{\hbar q}{4m^2c^2}\boldsymbol{\sigma}\cdot\left[\boldsymbol{\pi}\times\nabla\phi(\mathbf{r})\right]. \qquad \text{spin} - \text{orbit}
\end{aligned}
$$

these terms are independent of spin

Only the spin-orbit term couples the spin up and spin down Hamiltonians, and also relates the spin to the lattice degrees of freedom. Without the spin-orbit term, we do not need two-component spinors.

Solutions are two-component spinors

Fine Structure of Hydrogen

Kinetic energy term

potential energy term

$$\hat{H}^0 = \frac{\hat{p}^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$$

reduced mass of the electron-proton pair, to be more precise

Exact wavefunction: $\langle r, \theta, \phi | \tilde{\psi}^0_{n,l,m} \rangle = R_{nl}(r) Y_l^m(\theta, \phi)$

Exact eigenvalues: $E^0_{n,l,m} = -\left[\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2}$

highly degenerate because it is independent of (l, m) !!!

Fine Structure of Hydrogen Atom

in terms of the fine structure constant $\alpha \equiv \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137.036}$ $E^0_{n,l,m} = -\left[\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2}$

Bohr formula

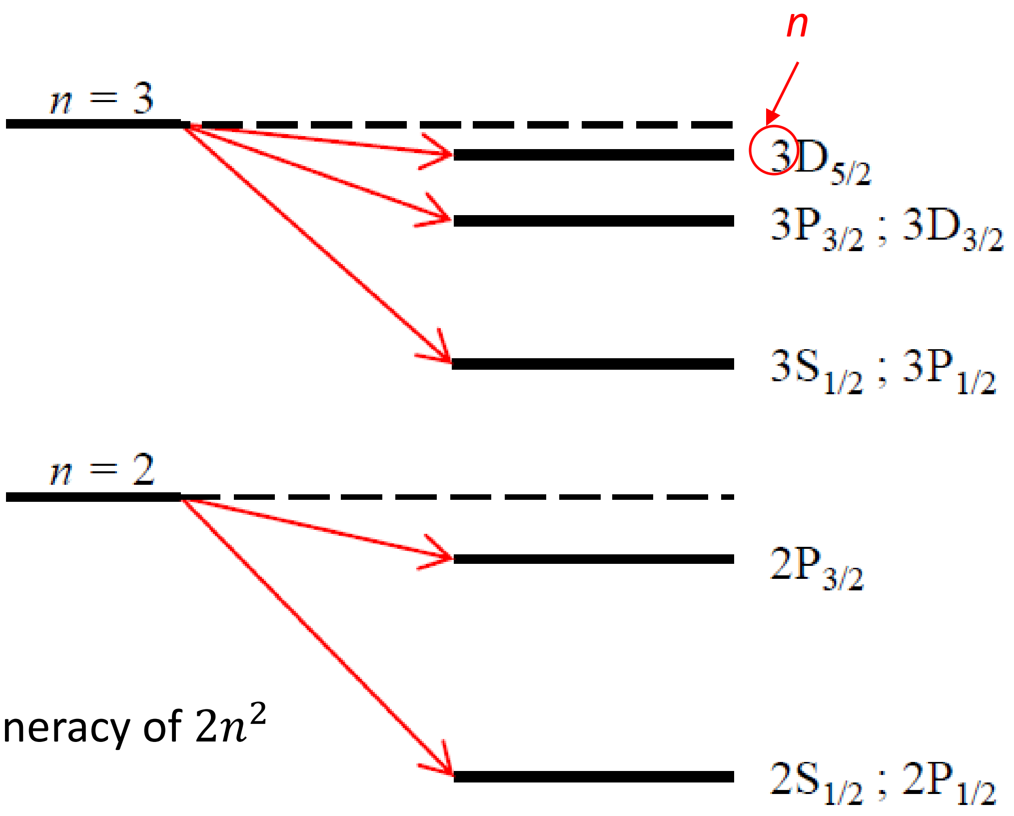
	Eigenvalues from the Bohr formula	$E_n = \alpha^2(m_e c^2)$
From Dirac's equation (without external fields)	Fine structure	$E_n\left(1+\frac{\alpha^2}{n^2}\left(\frac{n}{j+1/2}-\frac{3}{4}\right)\right)$
	- mass-velocity term	$E_n\frac{\alpha^2}{n^2}\left(\frac{n}{\ell+1/2}-\frac{3}{4}\right)$
	- spin-orbit coupling term	$E_n\frac{\alpha^2}{n^2}\frac{n[\frac{3}{4}+\ell(\ell+1)-j(j+1)]}{2\ell(\ell+\frac{1}{2})(\ell+1)}$ $\quad l \neq 0$
	- Darwin term	$-E_n\frac{\alpha^2}{n}$ $\quad$ Only for $l = 0$

depends on j only, i.e. for the same j, all m_j states have the same energy.

Term symbols and Hydrogen fine structure

$$^{n}L_{j}$$

For the single electron state, s = ½
Omitted in the notation below.



degeneracy of $2n^2$

degeneracy is partially lifted

states with the same *j* but different m_j or *l* have the same energy.

Besides hydrogen atoms…

The Pauli Hamiltonian contains the interaction of spin with an external magnetic field. For a particle in an external potential, or interacting with other particles, a spin-dependence can also be present via the exchange term. But the spin up and spin down Hamiltonians can be separated and solved independently.

$$\begin{aligned} H &= \boxed{H_{Pauli}} \\ &- \frac{p^4}{8m^3c^2} \qquad \text{mass} - \text{velocity} \\ &+ \frac{\hbar^2 q}{8m^2c^2}\nabla\cdot\nabla\phi(\mathbf{r}) \qquad \text{Darwin} \\ &- \frac{\hbar q}{4m^2c^2}\boldsymbol{\sigma}\cdot\left[\boldsymbol{\pi}\times\nabla\phi(\mathbf{r})\right]. \qquad \text{spin} - \text{orbit} \end{aligned}$$

these terms are independent of spin

Only the spin-orbit term couples the spin up and spin down Hamiltonians, and also relates the spin to the lattice degrees of freedom. Without the spin-orbit term, we do not need two-component spinors.

Solutions are two-component spinors

Spin-orbit term as a perturbation

Given an external potential and an approximation to the Hamiltonian, e.g. Hartree-Fock, how do we include the relativistic corrections?

$$
\begin{aligned}
H &= \boxed{H_{Pauli}} \\
&- \frac{p^4}{8m^3c^2} \qquad \text{mass} - \text{velocity} \\
&+ \frac{\hbar^2 q}{8m^2c^2}\nabla \cdot \nabla\phi(\mathbf{r}) \qquad \text{Darwin} \\
&- \frac{\hbar q}{4m^2c^2}\boldsymbol{\sigma} \cdot \left[\boldsymbol{\pi} \times \nabla\phi(\mathbf{r})\right]. \quad \text{spin} - \text{orbit}
\end{aligned}
$$

scalar relativistic approximation

includes these terms only. No spinors are needed.

The spin-orbit term couples the spin up and spin down Hamiltonians. It can be included as a perturbation to the scalar relativistic Hamiltonian.

Solutions are two-component spinors