1) 60(8): Helium Atom and Exchange Energy; Photon Absorption.

The helium atom (He) has two electrons and a nucleus of two protons. The Schrödinger equation describing it is:

$$\hat{H}\psi = E\psi \quad -(1)$$

where:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \quad -(2)$$

Here the ∇_1^2 and ∇_2^2 are the second derivatives with respect to the coordinates of the two electrons. The next two terms are electron-proton terms and the final term is the electron-electron term. The SE is therefore:

$$\hat{H}(\underline{r}_1, \underline{r}_2)\psi = E(\underline{r}_1, \underline{r}_2)\psi \quad -(3)$$

It is not possible to solve this analytically, so various levels of approximation are used. In perturbation theory, a first approximation is attempted, taking the perturbation as the electron-electron repulsion. The unperturbed hamiltonian $\hat{H}^{(0)}$ and the perturbed hamiltonian make up the right hand side of eq. (2). The unperturbed hamiltonian is:

$$H^{(0)} = H_1 + H_2, \quad H_i = -\frac{\hbar^2}{2m_e}\nabla_i^2 - \frac{2e^2}{4\pi\epsilon_0 r_i} \quad -(4)$$

where

$$H_i\psi(\underline{r}_i) = E_i\psi(\underline{r}_i) \quad -(5)$$

Thus:

$$\begin{aligned}(H_1 + H_2)\psi(\underline{r}_1, \underline{r}_2) &= (H_1 + H_2)\psi(\underline{r}_1)\psi(\underline{r}_2) \\ &= H_1\psi(\underline{r}_1)\psi(\underline{r}_2) + \psi(\underline{r}_1)H_2\psi(\underline{r}_2) \\ &= E_1\psi(\underline{r}_1)\psi(\underline{r}_2) + E_2\psi(\underline{r}_1)\psi(\underline{r}_2) \\ &= (E_1 + E_2)\psi(r_1, r_2) \quad -(6)\end{aligned}$$

2) The unperturbed wavefunction of He is therefore:

$$\phi(\underset{\sim}{r_1}, \underset{\sim}{r_2}) = \phi_{n_1 l_1 m_{l1}}(\underset{\sim}{r_1})\, \phi_{n_2 l_2 m_{l2}}(\underline{r_2}) \quad -(7)$$

with energy:

$$E = -4\hbar c R_\infty \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} \right) \quad -(8)$$

The electron-electron repulsion introduces the first order correction:

$$E^{(1)} = J = \left\langle n_1 l_1 m_{l1} ; n_2 l_2 m_{l2} \left| \frac{e^2}{4\pi\epsilon_0 r_{12}} \right| n_1 l_1 m_{l1} ; n_2 l_2 m_{l2} \right\rangle \quad -(9)$$

The Coulomb integral is:

$$J = \frac{e^2}{4\pi\epsilon_0} \int |\phi_1(\underset{\sim}{r_1})|^2 \frac{1}{r_{12}} |\phi_2(\underline{r_2})|^2 \, d\tau_1 \, d\tau_2 \quad -(10)$$

ECE Resonance Condition

In order to ionize the He atom it is possible to have a spin connection so that the following condition holds:

$$\left(\frac{e^2}{4\pi\epsilon_0 r_{12}} \right)_{\text{eff}} \gg \left(\frac{2e^2}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \right)_{\text{eff}} \quad -(11)$$

This means that the effective electron-electron repulsion becomes much greater than the effective electron-proton attraction. The repulsion term is governed by:

$$-\nabla^2 \phi(\underline{r_{12}}) + \underline{\omega} \cdot \underline{\nabla} \phi(\underline{r_{12}}) + (\underline{\nabla} \cdot \underline{\omega}) \phi(r_{12}) = \rho / \epsilon_0 \quad -(12)$$

3)

where $\phi(r_{12})$ is the repulsion potential. If the charge density is written as:

$$\rho = e / V \quad -(13)$$

the positive repulsion potential is:

$$V(r_{12}) = e\phi(r_{12}) \quad -(14)$$

At resonance $V(r_{12})$ and $\phi(r_{12})$ become very large and the He atom ionizes. However, in this situation the perturbation approach is invalidated, and a density functional approach is needed.

<u>Exchange Integral</u>

The wavefunctions of the exchange integral are: $-(15)$

$$\psi_{\pm}(\underline{r}_1, \underline{r}_2) = \frac{1}{\sqrt{2}}\left(\psi_1(\underline{r}_1)\psi_2(\underline{r}_2) \pm \psi_2(\underline{r}_1)\psi_1(\underline{r}_2)\right)$$

where ψ_1 and ψ_2 are H-like for $Z = 2$. The Coulombic electron-electron repulsion terms in this case remove the degeneracy of the two product functions, giving an energy separation $2K$. The integral K is the quantum correction to the Coulomb integral J. Both are affected by resonance in the Coulomb law. This is the basis for <u>Fermi</u> <u>Hole</u> theory. This is the amplitude $|\psi_-|^2$ vanishes when $\underline{r}_1 = \underline{r}_2$. This is the basis for semi-conductor theory, which is therefore affected by resonance in the Coulomb law. The helium atom is the simplest ~~at~~ atom in which the exchange integral occurs.

4) Atomic Absorption of a Photon by an Atom

As described by Marion and Thornton on pp. 120 ff. atomic systems can be represented classically as linear oscillators. When electromagnetic radiation falls on matter the atoms and molecules vibrate. A resonant frequency occurs at one of the spectral frequencies of the system. If the frequency of the light is the same as one of the resonant frequencies of the atomic or molecular system, electromagnetic energy is absorbed causing the atom or molecule to vibrate with large amplitude. Large electromagnetic fields of the same frequency are produced by the oscillating electric charges.

This process is described by eq. (21.26) of vol. 1 of ECE theory through the minimal prescription. In the presence of an electromagnetic field the ECE Lemma:

$$\Box q^c = R q^c \quad -(16)$$

is changed to:

$$\Box q^c = (R_1 + R_2 + R) q^c \quad -(17)$$

In the Dirac limit:

$$\left.\begin{aligned} |R_1| &= e^2 A_a^* A^a / \hbar^2 \\ |R_2| &= emc\, \gamma^a (A_a + A_a^*) / \hbar^2 \end{aligned}\right\} -(18)$$

This process is a minimal prescription in which $\underline{\nabla}$ is changed to $\underline{\nabla} - i\frac{e}{\hbar}\underline{A}$. Therefore in this case the spin connection is:

$$\underline{\omega} = -i\frac{e\underline{A}}{\hbar} \quad -(19)$$

$$= -ig\underline{A} \quad -(20)$$

5) The modulus of eq. (19) gives:

$$\hbar \kappa = e A^{(0)} \quad -(21)$$

where:

$$\kappa := |\underline{\omega}| \quad -(22)$$

is the magnitude of the spin connection. Eq. (21) corresponds to the absorption of a photon $\hbar\omega$. The angular momentum of the photon is $\pm\hbar$. It can be seen that the photon originates in the spin connection. The kinetic energy operator of the H atom is changed from

$$-\frac{\hbar^2}{2m}\nabla^2 \text{ to } -\frac{\hbar^2}{2m}\left(\underline{\nabla} - i\frac{e}{\hbar}\underline{A}\right)^2 = -\frac{\hbar^2}{2m}\left(\underline{\nabla} + \underline{\omega}\right)^2.$$

Thus:

$$\boxed{\nabla^2\phi \rightarrow \left((\underline{\nabla} + \underline{\omega})\cdot(\underline{\nabla} + \underline{\omega})\phi\right)} \quad -(23)$$

and we obtain a resonance eqn. $\quad -(24)$

$$\boxed{-\frac{\hbar^2}{2m}\left(\nabla^2 + \underline{\omega}\cdot\underline{\nabla} + \underline{\nabla}\cdot\underline{\omega} + \omega^2\right)\phi = (E - V)\phi}$$

where V is the Coulombic term. There are therefore resonances due to the absorption of a photon, and a novel type of resonance inside the Coulomb Law itself.