1) 86(10): The Coulomb Integral in Helium

Reference: P. W. Atkins, "Molecular Quantum Mechanics" (Oxford University Press, 1983, 2nd. ed.)

The Coulomb integral is:

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

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

The Coulombic interaction energy between two electrons in a hydrogen-like 1s orbital is evaluated using:

$$\phi(r_1) = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Z r_1 / a_0} \quad -(2)$$

$$\phi(r_2) = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Z r_2 / a_0} \quad -(3)$$

As described by Atkins on page 225, r_{12} is expanded in terms of r_1 and r_2. When $r_1 > r_2$:

$$\frac{1}{r_{12}} = \frac{1}{r_1} \sum_{l=0}^{\infty} \sum_{m_l=1}^{l} \left(\frac{4\pi}{2l+1}\right) \left(\frac{r_2}{r_1}\right)^l Y_{l m_l}(\theta_1, \phi_1) Y_{l m_l}(\theta_2, \phi_2) \quad -(4)$$

and when $r_2 > r_1$, interchange r_1 and r_2. The angular integration eliminates all terms in this sum except the one

2) with $l = m_l = 0$. The surviving term:

$$Y_{00} = \left(\frac{1}{4\pi}\right)^{1/2} \quad -(5)$$

Thus:

$$\frac{1}{r_{12}} = \frac{1}{r_1} \quad \text{when } r_1 > r_2, \quad -(6)$$

$$\frac{1}{r_{12}} = \frac{1}{r_2} \quad \text{when } r_2 > r_1. \quad -(7)$$

The radial integration is divided into two parts corresponding to $r_1 > r_2$ and $r_2 > r_1$. Thus:

$$J = \frac{e^2}{4\pi\epsilon_0}\left(\frac{Z^3}{\pi a_0^3}\right)^2 \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 \int_0^{\pi} \sin\theta_1 \, d\theta_1 \int_0^{\pi} \sin\theta_2 \, d\theta_2 \int \frac{r_1^2 r_2^2}{r_{12}} e^{-2Z(r_1+r_2)/a_0} \, dr_1 \, dr_2$$

$$= \frac{e^2}{4\pi\epsilon_0}\left(\frac{Z^3}{\pi a_0^3}\right)^2 (2\pi)^2 2^2 \int_0^{\infty} r_2^2 e^{-2Zr_2/a_0} \left(\int_0^{r_2} \frac{r_1^2}{r_2} e^{-2Zr_1/a_0} \, dr_1 + \int_{r_2}^{\infty} \frac{r_1^2}{r_1} e^{-2Zr_1/a_0} \, dr_1 \right) dr_2$$

$$\boxed{J = \frac{5}{8} \frac{e^2}{4\pi\epsilon_0} \frac{Z}{a_0}} \quad -(8)$$

For helium, $Z = 2$, so:

$$J = \frac{5}{4} \frac{e^2}{4\pi a_0} \quad -(9)$$

where

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} \quad -(10)$$

is the Bohr radius $(5.292 \times 10^{-11} \text{ m})$

Thus:

$$J = 5.45 \times 10^{-18} \text{ J} \quad — (11)$$

We have:

$$E_{1s} = -4hcR_\infty$$
$$= -8.72 \times 10^{-18} \text{ J} \quad — (12)$$

So the total energy of the atom is:

$$E = 2(-8.72 \times 10^{-18} \text{ J}) + 5.45 \times 10^{-18} \text{ J}$$
$$= -1.20 \times 10^{-17} \text{ J} \quad — (13)$$

This corresponds to -7220 kJ mole^{-1}. The experimental value is the sum of the first and second ionization energies of helium, and is -7619 kJ mole^{-1}. The perturbation is not small because:

$$J = \frac{5}{16}(2E_{1s}) \quad — (14)$$

so first order perturbation theory is not a good approximation.

<u>Radiative Correction</u> to <u>the Coulomb Integral</u>

These are calculated from the second line of eq. (8) using the radiative correction to r_1 and r_2, as given in note 86 (9a).

4) We recall that the radiative correction are calculated from:

$$-\frac{\hbar^2}{2m_e}\frac{d^2 P}{dr_1^2} - V^{(0)}_{eff,1} P = E_1 P \quad -(15)$$

$$-\frac{\hbar^2}{2m_e}\frac{d^2 P}{dr_2^2} - V^{(0)}_{eff,2} P = E_2 P \quad -(16)$$

where:

$$V^{(0)}_{eff,1} = -\frac{e^2}{2\pi\epsilon_0 r_1} + \frac{\ell(\ell+1)\hbar^2}{m r_1^2} \quad -(17)$$

$$V^{(0)}_{eff,2} = -\frac{e^2}{2\pi\epsilon_0 r_2} + \frac{\ell(\ell+1)\hbar^2}{m r_2^2} \quad -(18)$$

By hypothesis, eqs. (15) and (16) become:

$$-\frac{\hbar^2}{2m}\frac{d^2 P}{dr_1^2} - V_{eff,1} P = E_1 P \quad -(19)$$

$$-\frac{\hbar^2}{2m}\frac{d^2 P}{dr_2^2} - V_{eff,2} P = E_2 P \quad -(20)$$

after radiative corrections:

$$\frac{d^2}{dr_1^2} \rightarrow \left(1+\frac{\alpha}{4\pi}\right)^2 \frac{d^2}{dr_1^2} \quad -(21)$$

$$\frac{d^2}{dr_2^2} \rightarrow \left(1+\frac{\alpha}{4\pi}\right)^2 \frac{d^2}{dr_2^2} \quad -(22)$$

5) where:

$$\bar{V}_{eff,1} = \frac{e^2}{2\pi\epsilon_0(r_1 + r_{vac})} - \frac{\ell(\ell+1)\hbar^2}{(r_1 + r_{vac})^2} \quad -(23)$$

$$\bar{V}_{eff,2} = \frac{e^2}{2\pi\epsilon_0(r_2 + r_{vac})} - \frac{\ell(\ell+1)\hbar^2}{(r_2 + r_{vac})^2} \quad -(24)$$

To first order in α:

$$-\frac{\hbar^2\alpha}{4\pi m_e}\frac{d^2\rho}{dr_1^2} = \left(\bar{V}^{(0)}_{eff,1} - \bar{V}_{eff,1}\right)\rho \quad -(25)$$

$$-\frac{\hbar^2\alpha}{4\pi m_e}\frac{d^2\rho}{dr_2^2} = \left(\bar{V}^{(0)}_{eff,2} - \bar{V}_{eff,2}\right)\rho \quad -(26)$$

and for two 1s electrons:

$$J = \frac{e^2}{4\pi\epsilon_0}\left(\frac{Z^3}{\pi a_0^3}\right)^2(2\pi)^2 Z^2 \int_0^\infty r_2^2 e^{-2Zr_2/a_0}\left(\int_0^{r_2}\frac{r_1^2}{r_2}e^{-2Zr_1/a_0}dr_1 + \int_{r_2}^\infty \frac{r_1^2}{r_1}e^{-2Zr_1/a_0}dr_1\right)dr_2$$

$$-(27)$$

So the computer algebra should calculate r_1 and r_2 from eqs. (25) and (26) in terms of r_{vac} and express J as a function of r_{vac} in eq. (27). This shows how the vacuum affects 1s electron-electron repulsion.