1 Frozen-Core Hartree-Fock Potential

We consider a molecule $\Psi^{(\sigma\pi m)}$ which has spin σ, parity π, projection m and is composed of N occupied spin orbitals $\{{\chi^{(m)}}_n\}_{n=1}^{N}$. To ensure the total spin of the molecule is a conserved quantity, we assume that the spin orbitals are formed from a set of doubly-occupied spatial orbitals, $\{{\Omega^{(m)}}_n\}_{n=1}^{N/2}$. Furthermore, we suppose that each of these spatial orbitals can be expanded in partial waves

$$ {\Omega^{(m)}}_n(r,\theta,\phi) = \sum_{\ell=0}^{\infty} \omega_{n\ell}(r) Y_{\ell m}\left(\theta,\phi\right) $$

where $\omega_{n\ell}$ are referred to as the partial waves, and $Y_{\ell m}$ are the spherical harmonics.

We consider the case where an electron $\Phi^{(\sigma')}$, with spin σ', interacts with this molecule. To do so, we suppose that the electron can be expanded in terms of a basis the electronic state can be expanded in terms of a basis $\{\phi_\alpha = \xi_{k_\alpha \ell_\alpha}(r) Y_{\ell_\alpha m_\alpha}\left(\theta,\phi\right)\}$ and consider how the basis elements interact with the molecule.

1.1 Local Coulomb Potential

Coulombic interaction between basis elements and the electrons in the molecule give rise to matrix elements of the form

$$ J_{\alpha\beta} = \langle \phi_\alpha | \hat{J} | \phi_\beta \rangle = 2 \sum_{n=1}^{N/2} \langle \phi_\alpha {\Omega^{(m)}}_n | \phi_\beta {\Omega^{(m)}}_n \rangle $$

where

$$ \langle \phi_\alpha {\Omega^{(m)}}_n | \phi_\beta {\Omega^{(m)}}_n \rangle = \sum_{l_1=0}^{\infty} \sum_{l_2=0}^{\infty} \sum_{\lambda=0}^{\infty} \sum_{\mu=-\lambda}^{\lambda} \langle \xi_{k_\alpha \ell_\alpha} \omega_{n\ell_1} | \frac{r_<^\lambda}{r_>^{\lambda+1}} | \xi_{k_\beta \ell_\beta} \omega_{n\ell_2} \rangle \, \langle Y_{\ell_\alpha \rho_\alpha} \, | C_{\lambda\mu} | Y_{\ell_\beta \rho_\beta} \, \rangle \, \langle Y_{\ell_1 m} \, | {C_{\lambda\mu}}^\dagger | Y_{\ell_2 m} \, \rangle $$

and where $C_{\lambda\mu}$ is the irreducible spherical harmonic. However, by introducing a potential expanded through partial waves in the following form

$$ V_{\lambda\mu}\left(r\right) = 2 \sum_{n=1}^{N/2} \sum_{l_1=0}^{\infty} \sum_{l_2=0}^{\infty} \langle Y_{\ell_1 m} \, | {C_{\lambda\mu}}^\dagger | Y_{\ell_2 m} \, \rangle \left(\int_0^\infty \omega_{n\ell_1}(r') \frac{\min(r,r')^\lambda}{\max(r,r')^{\lambda+1}} \omega_{n\ell_2}(r') r'^2 \, \mathrm{d}r' \right) $$

we may write

$$ J_{\alpha\beta} = \sum_{\lambda=0}^{\infty} \sum_{\mu=-\lambda}^{\lambda} \langle \xi_{k_\alpha \ell_\alpha} | V_{\lambda\mu} \, | \xi_{k_\beta \ell_\beta} \rangle \, \langle Y_{\ell_\alpha \rho_\alpha} \, | C_{\lambda\mu} | Y_{\ell_\beta \rho_\beta} \, \rangle \, . $$

Note that as a result of constraints on the Wigner 3-j symbol, the partial waves are non-vanishing only for $\mu = 0$, so only $V_{\lambda 0}$ is of concern.

1.2 Non-Local Exchange Potential

Fermionic behaviour of electrons introduces a non-local coulombic interaction, known as the exchange potential. The matrix elements for this potential are given by

$$K_{\alpha\beta} = \langle\phi_\alpha|\hat{K}|\phi_\beta\rangle = \sum_{n=1}^{N/2} \langle\phi_\alpha {\Omega^{(m)}}_n|\Omega^{(m)}{}_n\phi_\beta\rangle$$

where

$$\langle\phi_\alpha {\Omega^{(m)}}_n|\Omega^{(m)}{}_n\phi_\beta\rangle = \sum_{l_1=0}^{\infty}\sum_{l_2=0}^{\infty}\sum_{\lambda=0}^{\infty}\sum_{\mu=-\lambda}^{\lambda} \langle\xi_{k_\alpha\ell_\alpha}\omega_{n\ell_1}|\frac{r_<^\lambda}{r_>^{\lambda+1}}|\omega_{n\ell_2}\xi_{k_\beta\ell_\beta}\rangle \langle Y_{\ell_\alpha\rho_\alpha}|C_{\lambda\mu}|Y_{\ell_2 m}\rangle \langle Y_{\ell_1 m}|{C_{\lambda\mu}}^\dagger|Y_{\ell_\beta\rho_\beta}\rangle .$$

A radial potential cannot be introduced to simplify the calculation of these elements due to the non-locality of the interaction.