CIS

February 5, 2019

1 CIS Equations in the Jellium AO Basis

The CIS wavefunction can be written as

$$\Psi_{CIS} = c_0|\Phi_0\rangle + \sum_{i,a} c_i^a |\Phi_i^a\rangle \tag{1}$$

where $|\Phi_0\rangle$ is the Hartree-Fock reference and and $|\Phi_i^a\rangle$ are singly-excited determinants. The CIS Hamiltonian Matrix has three classees of terms:

$$\langle\Phi_0|\hat{H}|\Phi_0\rangle = E_0, \tag{2}$$

$$\langle\Phi_0|\hat{H}|\Phi_i^a\rangle = \langle\phi_i|\hat{h}|\phi_a\rangle + \sum_k \langle\phi_i\phi_k||\phi_a\phi_k\rangle, \tag{3}$$

and

$$\langle\Phi_i^a|\hat{H}|\Phi_j^b\rangle = E_0\delta_{ij}\delta_{ab} + \left(\langle\phi_a|\hat{h}|\phi_b\rangle + \sum_k \langle\phi_a\phi_k||\phi_b\phi_k\rangle\right)\delta_{ij} - \left(\langle\phi_i|\hat{h}|\phi_j\rangle + \sum_k \langle\phi_i\phi_k||\phi_j\phi_k\rangle\right)\delta_{ab} + \langle\phi_a\phi_j||\phi_i\phi_b\rangle. \tag{4}$$

The 1- and 2-electron integrals above are expressed in the MO basis, and each MO can be expressed as a linear combination of AOs:

$$\phi_n = \sum_\mu c_\mu^n \psi_\mu \tag{5}$$

where

$$\psi_\mu = \left(\frac{2}{\pi}\right)^{3/2} \sin\left(\mu_x x\right)\sin\left(\mu_y y\right)\sin\left(\mu_z z\right). \tag{6}$$

Consider the 1-electron integrals of the form $\langle\phi_a|\hat{h}|\phi_b\rangle$; they can be expressed as linear combinations of the AO integrals as follows:

$$\left(\sum_{\mu,\nu} c_\mu^a c_\nu^b \frac{\delta_{\mu,\nu}}{2}\left(\mu_x^2+\mu_y^2+\mu_z^2\right)\right) + \left(n\sum_{\mu,\nu} c_\mu^a c_\nu^b V_{\mu,\nu}\right) \tag{7}$$

where the terms in the first sum only survive when $\mu = \nu$ and the terms in the second sum only survive when the pairs $(\mu_x,\nu_x), (\mu_y,\nu_y), (\mu_z,\nu_z)$ have the same parity. Thus, the first sum reduces to

$$\sum_{\mu} c^{a}_{\mu} c^{a}_{\mu} \frac{1}{2} \left(\mu_x^2 + \mu_y^2 + \mu_z^2 \right) \tag{8}$$

and somehow the second sum contains many fewer terms than you would expect, but need to figure out how much fewer more precisely!