Computational Physics II
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Abstract

Fill in abstract

1 Introduction

2 Methods

2.1 Derivation of local energies

The local energy of is dependant on the Hamiltonian and the wavefunction describing the system, the Hamiltonian incorporates both a kinetic energy part given by $\frac{\nabla_i^2}{2}$ for each particle and a potential energy part given by $\frac{Z}{r_i}$ and $\frac{1}{r_{ij}}$, where Z is the charge of the center, r_i is the distance for electron i to the atom center and r_{ij} is the distance between electron l and m. Then the local energy is given by the following:

$$E_L = \sum_{i,i<j} \frac{1}{\Psi_T(\mathbf{r_i}, \mathbf{r_{ij}})} \hat{H} \Psi_T(\mathbf{r_i}, \mathbf{r_{ij}}) \tag{1}$$

$$= \sum_{i,i<j} \frac{1}{\Psi_T(\mathbf{r_i}, \mathbf{r_{ij}})} \left(-\frac{\nabla_i^2}{2} - \frac{Z}{r_i} - \frac{Z}{r_j} + \frac{1}{r_{ij}} \right) \Psi_T(\mathbf{r_i}, \mathbf{r_{ij}}) \tag{2}$$

$$= \sum_{i,i<j} -\frac{1}{2\Psi_T} \left(\nabla_i^2 \Psi_T \right) - \frac{Z}{r_i} - \frac{Z}{r_j} + \frac{1}{r_{ij}} \tag{3}$$

Let us change derivation variables:

$$-\frac{1}{2\Psi_T} \left(\nabla_i^2 \Psi_T \right) = \sum_{m=1}^{3} -\frac{1}{2\Psi_T} \left(\frac{\partial^2 \Psi_T}{\partial x_m^2} \right)_i \tag{4}$$

$$= \sum_{m=1}^{3} -\frac{1}{2\Psi_T} \left(\frac{\partial}{\partial x_m} \left(\frac{\partial \Psi_T}{\partial r_i} \frac{\partial r_i}{\partial x_m} \right) \right)_i \tag{5}$$

Since $r_i = \left(x_1^2 + x_2^2 + x_3^2\right)^{1/2}$ then $\frac{\partial r_i}{\partial x_m} = \frac{\partial\left(x_1^2+x_2^2+x_3^2\right)^{1/2}}{\partial x_m} = \frac{x_m}{r_i}$

$$= \sum_{m=1}^{3} -\frac{1}{2\Psi_T}\left(\frac{\partial}{\partial x_m}\left(\frac{\partial \Psi_T}{\partial r_i}\frac{x_m}{r_i}\right)\right)_i \tag{6}$$

$$= \sum_{m=1}^{3} -\frac{1}{2\Psi_T}\left(\frac{\partial^2 \Psi_T}{\partial x_m \partial r_i}\frac{x_m}{r_i} + \frac{\partial \Psi_T}{\partial r_i}\frac{\partial}{\partial x_m}\left(\frac{x_m}{r_i}\right)\right)_i \tag{7}$$

The term $\frac{\partial}{\partial x_m}\left(\frac{x_m}{r_i}\right)$ becomes for the different values for m, $\frac{\partial}{\partial x_1}\left(\frac{x_1}{\left(x_1^2+x_2^2+x_3^2\right)^{1/2}}\right) = \frac{x_2^2+x_3^2}{r_i^3}$ so all the values for m term it should sum up to $\frac{2(x_1^2+x_2^2+x_3^2)}{r_i^3}$

$$= -\frac{1}{2\Psi_T}\left(\frac{\partial^2 \Psi_T}{\partial r_i^2}\frac{x_1^2+x_2^2+x_3^2}{r_i^2} + \frac{\partial \Psi_T}{\partial r_i}\frac{2(x_1^2+x_2^2+x_3^2)}{r_i^3}\right)_i \tag{8}$$

$$= -\frac{1}{2\Psi_T}\left(\frac{\partial^2 \Psi_T}{\partial r_i^2} + \frac{\partial \Psi_T}{\partial r_i}\frac{2}{r_i}\right) \tag{9}$$

Then the local energy becomes:

$$E_L = \sum_{i,i<j} -\frac{1}{2\Psi_T}\left(\frac{\partial^2 \Psi_T}{\partial r_i^2} + \frac{\partial \Psi_T}{\partial r_i}\frac{2}{r_i}\right) - \frac{Z}{r_i} - \frac{Z}{r_j} + \frac{1}{r_{ij}} \tag{10}$$

2.1.1 Helium: Simple trialfunction

The simple version of the trial function is only dependant on one parameter α and does not take into account interaction between the two electrons, it is of the form

$$\Psi_T(\mathbf{r_1}, \mathbf{r_2}) = \exp\{-\alpha(r_1 + r_2)\}$$

Let us set this trialfunction into the equation for the local energy (10).

$$E_L = \sum_{i,i<j} -\frac{1}{2\Psi_T}\left(\frac{\partial^2 e^{-\alpha(r_i+r_j)}}{\partial r_i^2} + \frac{\partial e^{-\alpha(r_i+r_j)}}{\partial r_i}\frac{2}{r_i}\right) - \frac{Z}{r_i} - \frac{Z}{r_j} + \frac{1}{r_{ij}} \tag{11}$$

$$E_L = -\frac{1}{2\Psi_T}\sum_{i=1}^{2}\left(\alpha^2 - \alpha\frac{2}{r_i}\right)\Psi_T - \frac{Z}{r_i} + \frac{1}{r_{ij}} \tag{12}$$

$$E_L = -\alpha^2 + (\alpha - Z)\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{r_{12}} \tag{13}$$

3 Results and discussion

4 Conclusions and perspectives

The local energy for the simple trialfunct

$$Z\left(-\frac{1}{r_2} - \frac{1}{r_1}\right) - \alpha^2 + \alpha\left(\frac{1}{r_2} + \frac{1}{r_1}\right) + \frac{1}{r_{12}}$$