# Chem 195: Problem Set 7

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## Problem 1

i) $\hat{\Psi}(x,y) = a\chi_1(x)\chi_1(y) + b\chi_1(x)\chi_j(y)$

$= \chi_1(x)\left[a\chi_1(y) + b\chi_j(y)\right]$

So $\hat{\Psi}(x,y) = f(x)g(y)$ where $f(x) = \chi_1(x)$

$g(y) = a\chi_1(y) + b\chi_j(y)$

ii) Recall the antisymmetric $|\chi_i\chi_j\rangle$ is

$\left[\chi_i(x)\chi_j(y) - \chi_j(x)\chi_i(y)\right]/\sqrt{2}$

So for our superposition wavefn

$\hat{\Psi}(x,y) = a|\chi_1\chi_1\rangle + b|\chi_1\chi_j\rangle$

$= a\left[\cancel{\chi_1(x)\chi_1(y) - \chi_1(x)\chi_1(y)}\right]/\sqrt{2} + b\left[\chi_1(x)\chi_j(y) - \chi_j(x)\chi_1(y)\right]/\sqrt{2}$

$= \frac{b}{\sqrt{2}}\left[\chi_1(x)\chi_j(y) - \chi_j(x)\chi_1(y)\right]$

which is of the uncorrelated form we want

iii) The eigenvalue $E$ of $\mathcal{H}$ is given by

$$\det\begin{pmatrix} -E & \Delta \\ \Delta & \varepsilon - E \end{pmatrix} = 0$$

$-(E)(\varepsilon - E) - \Delta^2 = 0$

$E^2 - \varepsilon E - \Delta^2 = 0$

$E_+ = \frac{\varepsilon + \sqrt{\varepsilon^2 + 4\Delta^2}}{2}$ $\qquad E_- = \frac{\varepsilon - \sqrt{\varepsilon^2 + 4\Delta^2}}{2}$

$E_+ > \frac{\varepsilon + \varepsilon}{2} = \varepsilon$ $\qquad E_- < \frac{\varepsilon - \varepsilon}{2} = 0$

given that $\sqrt{\varepsilon^2 + 4\Delta^2} > \varepsilon$

iv) If the matrix element $\langle\chi_1\chi_j|\mathcal{H}|\chi_1\chi_1\rangle \neq 0$, that means we would have some nonzero coupling btw $|\chi_1\chi_1\rangle$ and $|\chi_1\chi_j\rangle$. That would mean that our ground state energy $E_{11}$ could be further split, resulting in an even lower ground state energy. However this is a contradiction, since $|\chi_1\chi_1\rangle$ is by construction the uncorrelated wavefn w/the lowest possible energy.

So $\langle\chi_1\chi_j|\mathcal{H}|\chi_1\chi_1\rangle = 0$

## Problem 2

i) $\langle x_i x_j | \mathcal{H} | x_k x_\ell \rangle$

$= \frac{1}{2}\left[ \langle x_i x_j | h(x) | x_k x_\ell \rangle + \langle x_i x_j | h(y) | x_k x_\ell \rangle + \langle x_i x_j | a x^4 y^4 | x_k x_\ell \rangle \right]$

- $\langle x_i x_j | h(x) | x_k x_\ell \rangle = \langle x_i x_j - x_j x_i | h(x) | x_k x_\ell - x_\ell x_k \rangle$

$= \langle x_i x_j | h(x) | x_k x_\ell \rangle - \langle x_j x_i | h(x) | x_k x_\ell \rangle$

$+ \langle x_j x_i | h(x) | x_\ell x_k \rangle - \langle x_i x_j | h(x) | x_\ell x_k \rangle$

$= \langle x_j | x_\ell \rangle \langle x_i | h(x) | x_k \rangle - \langle x_i | x_\ell \rangle \langle x_j | h(x) | x_k \rangle$

$+ \langle x_i | x_k \rangle \langle x_j | h(x) | x_\ell \rangle - \langle x_j | x_k \rangle \langle x_i | h(x) | x_\ell \rangle$

- Similary for $h(y)$

$\langle x_i x_j | h(y) | x_k x_\ell \rangle = \langle x_j | x_\ell \rangle \langle x_i | h(y) | x_k \rangle - \langle x_i | x_\ell \rangle \langle x_j | h(y) | x_k \rangle$
$+ \langle x_i | x_k \rangle \langle x_j | h(y) | x_\ell \rangle - \langle x_j | x_k \rangle \langle x_i | h(y) | x_\ell \rangle$

IF Fact $\langle x_i x_j | h(x) | x_k x_\ell \rangle = \langle x_i x_j | h(y) | x_k x_\ell \rangle$

- $\langle x_i x_j - x_j x_i | x^4 y^4 | x_k x_\ell - x_\ell x_k \rangle$

$= \langle ij | x^4 y^4 | k\ell \rangle - \langle ij | x^4 y^4 | \ell k \rangle - \langle ji | x^4 y^4 | k\ell \rangle + \langle ji | x^4 y^4 | \ell k \rangle$

$= \langle i | x^4 | k \rangle \langle j | y^4 | \ell \rangle - \langle i | x^4 | \ell \rangle \langle j | y^4 | k \rangle - \langle j | x^4 | k \rangle \langle i | y^4 | \ell \rangle + \langle j | x^4 | \ell \rangle \langle i | y^4 | k \rangle$

Since $\langle i | x^4 | k \rangle = \langle i | y^4 | k \rangle \ldots$

$= 2 \langle i | x^4 | k \rangle \langle j | x^4 | \ell \rangle - 2 \langle i | x^4 | \ell \rangle \langle j | x^4 | k \rangle$

Putting it all together we get

$$\langle ij|\mathcal{H}|kl\rangle = \frac{1}{2}\left[2\langle ij|h(x)|kl\rangle + a\langle ij|x^4y^4|kl\rangle\right.$$

$$= \langle j|l\rangle\langle i|h(x)|k\rangle - \langle i|l\rangle\langle j|h(x)|k\rangle + \langle i|k\rangle\langle j|h(x)|l\rangle$$
$$- \langle j|k\rangle\langle i|h(x)|l\rangle$$
$$+ a\left[\langle i|x^4|k\rangle\langle j|x^4|l\rangle - \langle i|x^4|l\rangle\langle j|x^4|k\rangle\right]$$

ii) When we expand the orbitals and write everything in matrix notation we note that

$$\langle j|l\rangle = \delta_{jl}$$

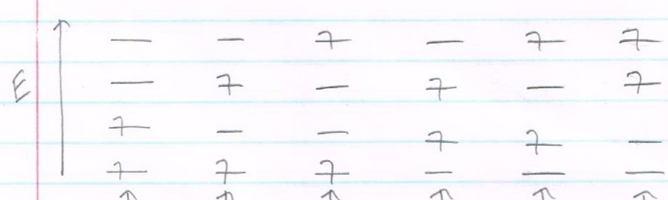
$$\langle i|h(x)|k\rangle = \underline{c_i}\cdot\underline{\underline{h}}\cdot\underline{c_k}$$

$$\langle i|x^4|k\rangle = \underline{c_i}\cdot\underline{\underline{G}}\cdot\underline{c_k}$$

Thus we can rewrite our previous answer as follows

$$\langle ij|\mathcal{H}|kl\rangle = \delta_{jl}\, c_i\cdot h\cdot c_k - \delta_{il}\, c_j\cdot h\cdot c_k + \delta_{ik}\, c_j\cdot h\cdot c_l - \delta_{jk}\, c_i\cdot h\cdot c_l$$
$$+ a\left[(c_i\cdot G\cdot c_k)(c_j\cdot G\cdot c_l) - (c_i\cdot G\cdot c_l)(c_j\cdot G\cdot c_k)\right]$$

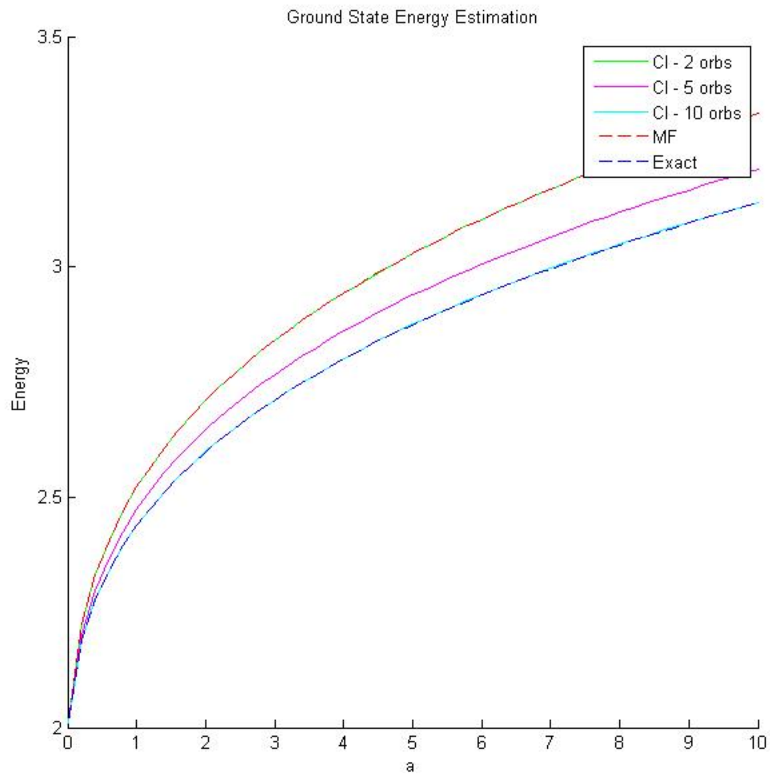
iii) For $N_{orb} = 4$, there are 6 distinct, allowed configurations




iv) ① ② ③ ④ ⑤ ⑥

This indexing is reflected in my code in "CIOscfunc.m" at line 69

For $N_{orb} = 4$, the CI method gives us a ground state energy of $2.4870 Hartrees$ for an anharmonic factor of $a = 1.0$. Below is a plot depicting ground state energies as a function of the anharmonic factor $a \in [0, 10]$:




From the plot we see that the CI results when we use only two orbitals are exactly the same as the mean field results. This is unsurprising because when $N_{orb} = 2$ for our CI method, that means that there is only one configuration that is possible (i.e. the symmetry-constrained mean field ground state).

We also see that as we increase the number of orbitals for our CI calculations, we approach the "exact" solution. In fact when by the time we reach $N_{orb} = 10$ the ground state energies are essentially the same as the "exact" values, attesting to the accuracy of the CI method.