HOMEWORK ASSIGNMENT 4
QUANTUM MECHANICS
DUE FEB 26, 2008

SILVIO LEVY

1a. *Prove that the MP2 energy is size-consistent for two infinitely separated closed shell fragments.*

The MP2 energy is the sum of the Hartree-Fock energy (whose size-consistency we know) and the second-order correction, given by

$$E_0^{(2)} = \langle \Psi_0^{(0)} | V^{(1)} | \Psi_0^{(1)} \rangle = \frac{1}{4} \sum_{i,j}^{\text{(occup)}} \sum_{a,b}^{\text{(virt)}} \frac{|\langle ij \| ab \rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}. \qquad (*)$$

Now, if a system is composed of two fragments A and B very far apart, we can separate the HF orbitals (both occupied and virtual) into two classes: those supported in the fragment A and those supported in B. The double sum on the right unfolds into

$$\Biggl(\sum_{i,j\in A}^{\text{(occup)}} \sum_{a,b\in A}^{\text{(virt)}} + \sum_{\substack{i\in A\\ j\in B}}^{\text{(occup)}} \sum_{a,b\in A}^{\text{(virt)}} + \cdots + \sum_{i,j\in B}^{\text{(occup)}} \sum_{a,b\in B}^{\text{(virt)}} \Biggr) \frac{|\langle ij \| ab \rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b},$$

where the dots stand for 13 "mixed" sums similar to the second (at least one of i, j is supported on a different fragment from at least one of a, b). We claim that for all 14 mixed sums, the term $\langle ij \| ab \rangle := (ia|jb) - (ib|ja)$ vanishes. There are a few cases to consider:

- Exactly one of i, j, a, b belongs to A and the other three to B (eight cases). For example, suppose that $i \in A$ and $a, b \in B$; then $(ia|jb) = 0$, because for any $\boldsymbol{x}_1$, either $\chi_i(\boldsymbol{x}_1) = 0$ or $\chi_a(\boldsymbol{x}_1) = 0$. Similarly, $(ib|ja)$ vanishes.
- The same argument works if $i, j \in A$ and $a, b \in B$, or vice versa (two cases).
- Finally we can have i, j in different fragments, and likewise for a, b. For instance, take $i, a \in A$ and $j, b \in B$. Here the preceding argument fails for

$$(ia|jb) = \int \chi_i(\boldsymbol{x}_1)\chi_a(\boldsymbol{x}_1) \frac{1}{|\boldsymbol{x}_1 - \boldsymbol{x}_2|} \chi_j(\boldsymbol{x}_2)\chi_b(\boldsymbol{x}_2)\, d\boldsymbol{x}_1\, d\boldsymbol{x}_2,$$

  but this integral vanishes nonetheless, because the distance is infinite for pairs $(\boldsymbol{x}_1, \boldsymbol{x}_2)$ such that the products to the right and left are nonzero.

Thus all summands vanish except the first and last:

$$E_0^{(2)} = \Biggl(\sum_{i,j\in A}^{\text{(occup)}} \sum_{a,b\in A}^{\text{(virt)}} + \sum_{i,j\in B}^{\text{(occup)}} \sum_{a,b\in B}^{\text{(virt)}} \Biggr) \frac{|\langle ij \| ab \rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} = E_{0,A}^{(2)} + E_{0,B}^{(2)}.$$

1b. *Explicitly write out the MP2 energy correction to a single determinant of spin-orbitals which does not satisfy the Brillouin condition.*

In this case we must add to the right-hand side of $(*)$ of 1a the contribution of single excitations, which is

$$\langle \Psi_0 | V^{(1)} | \Psi_S \rangle = \sum_{i \text{ occ}} \sum_{a \text{ virt}} \langle \Psi_0 | V^{(1)} | \Psi_i^a \rangle =$$