

Spring Semester 2006

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(Some material in this lecture has been adapted from Cramer, C. J. *Essentials of Computational Chemistry*, Wiley, Chichester: 2002; pp. 201-203; 207-210; 216; 220-222.)

Solved Homework

With only two CSFs to consider, we determine the energies from

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0$$

The two-by-two determinant is easy to expand: it is

$$E^2 - (H_{11} + H_{22})E + (H_{11}H_{22} - H_{12}^2) = 0$$

where we've replaced H_{21} with H_{12} (they are equal since H is hermitian). This is a quadratic equation in E , so it has roots determined from the quadratic formula, namely

$$\begin{aligned} E &= \frac{(H_{11} + H_{22}) \pm \sqrt{(H_{11} + H_{22})^2 - 4(H_{11}H_{22} - H_{12}^2)}}{2} \\ &= \frac{(H_{11} + H_{22}) \pm \sqrt{H_{11}^2 - 2H_{11}H_{22} + H_{22}^2 + 4H_{12}^2}}{2} \\ &= \frac{(H_{11} + H_{22}) \pm \sqrt{(H_{11} - H_{22})^2 + 4H_{12}^2}}{2} \end{aligned}$$

Now consider what this equation says. The two energies are the average of the individual single-determinantal state energies H_{11} and H_{22} (the part before the \pm) plus or minus one-half the square root of the square of the *difference* between the two state energies plus something that must be non-negative. Note that if H_{12} is zero, then the two roots are just H_{11} and H_{22} , i.e., if there is no off-diagonal coupling between the states, there is no advantage to doing a CI with the two states. But, when it is positive, it will cause the root derived from subtracting the square root term from the average state energy to fall *below* H_{11} .

So, what is H_{12} ? It's an easy matter to determine given the simplicity of the ground- and excited-state determinants. We evaluate it as

$$\begin{aligned} H_{12} &= \langle \sigma(1)\sigma(2) | H | \sigma^*(1)\sigma^*(2) \rangle \\ &= \left\langle \sigma(1)\sigma(2) \left| \frac{1}{r_{12}} \right| \sigma^*(1)\sigma^*(2) \right\rangle \\ &= K_{\sigma\sigma^*} \end{aligned}$$

All of the one-electron integrals in the expectation value of the Hamiltonian must be zero since if it is a one-electron term for electron 1, the integral over electron 2 is the overlap integral of σ and orthogonal σ^* , and if it is a one-electron term for electron 2, the integral over electron 1 must be zero for the same reason. The only term that survives is the electron-electron repulsion integral, which in this case corresponds to the exchange integral between the two orbitals.

Limited Configuration Interaction

We left off last time considering the structure of the CI matrix \mathbf{H} which must be diagonalized to find the improved ground-state energy compared to the HF energy.

What if we only keep single excitations? In that case, we see from the last figure in Lecture 37 that the CI matrix will be so-called block diagonal. One “block” will be the HF energy, H_{11} , and the other will be the singles/singles region. Since a block diagonal matrix can be fully diagonalized block by block, and since the HF result is already a block by itself, it is apparent that the lowest energy root, i.e., the ground-state HF root, is *unaffected* by inclusion of single excitations. Indeed, one way to think about the HF process is that it is an optimization of orbitals subject to the constraint that single-excitations do *not* contribute to the wave function. Thus, the so-called CI singles (CIS) method finds no use for improving ground state energies. It *can*, however, be useful for computing excited state energies. These are the second and higher eigenvalues of the CI matrix. Just as in HF theory there are as many orbitals as basis functions, each characterized by a different energy, so too in CI calculations there are as many states as there are starting configuration state functions, each characterized by a particular energy.

So, we might next consider including only double excitations (CID). In fact, the homework for H_2 above was a CID calculation. We have already noted that the ground state energy from that solution is lower than the HF energy. The magnitude of that difference (which is called the correlation energy, E_{corr}) with the STO-3G basis set at a bond distance of 1.4 a.u. is -0.02056 a.u., or about 13 kcal/mol. That's quite a bit from a chemical point of view!

In bigger systems, this process can be carried out analogously. However, the size of the CI matrix can quickly become very, very large, in which case diagonalization is

computationally taxing (diagonalizing a matrix scales as the dimension of the matrix cubed; since a standard CI matrix may have as many as 100,000 or more rows/columns, this can be an enormous task). More efficient methods than diagonalization exist for finding only one or a few eigenvalues of large matrices. These methods are typically iterative, and most modern electronic structure programs use them in preference to full matrix diagonalization.

What about triple excitations? While there are no non-zero matrix elements between the ground state and triply-excited states, the triples do mix with the doubles, and can through them influence the lowest energy eigenvalue. So, there is some motivation for including them. On the other hand, there are a *lot* of triples, making their inclusion difficult in a practical sense. As a result, triples, and higher-level excitations, are usually not accounted for in truncated CI treatments.

Let us return, however, to singly-excited determinants. While, like triples, they fail to interact with the ground state (in their case because of Brillouin's theorem), they too can mix with doubles and thus can have *some* influence on the lowest eigenvalue. In this instance, there are sufficiently few singles compared to doubles that it does not make the problem significantly more difficult to include them, and this level of theory is known as CISD.

The scaling for CISD with respect to system size is, in the large basis limit, on the order of N^6 where N is the number of basis functions. Such scaling behavior is considerably worse than HF (N^4 , remember), and thus poses a more stringent limit on the sizes of systems that can be practically addressed. To save time in CISD calculations, some orbitals can be frozen in the generation of excited states. A popular choice is to leave the core orbitals frozen in CISD.

One of the most appealing features of CISD is that it is variational. Thus, the CISD energy represents an upper bound on the exact energy. However, it has a particularly unattractive feature as well, and that is that it is not "size extensive". This property is best explained by example: consider the H_2 molecule case addressed above. We may construct the CID wave function as

$$\Psi_{\text{CID}} = (1-c)^2 \Psi_{\text{HF}} + c^2 \Psi_{1\bar{1}}^{2\bar{2}} \quad (38-1)$$

where the coefficient c is determined from the diagonalization process. Now, consider the CID wave function for two molecules of H_2 separated by, say, 50 Å. For all practical purposes, there is no chemical interaction between them, so we could take the overall wave function simply to be a properly antisymmetrized product of eq. 38-1 with itself. This expression would include a term, preceded by the coefficient c^4 , corresponding to simultaneous double excitation within each molecule. However, that is a quadruply excited configuration. As such, if we carried out a CID calculation on the two molecules as a single system, it would not be permitted. Thus, twice the CID energy of one molecule of H_2 will be lower than the CID energy for two molecules of H_2 at large

separations, which is a vexing result. In modern work, there has been a tendency to avoid single-reference CI calculations in favor of other, size-extensive methods for including electron correlation, including perturbation theory, which we turn to next.

Møller-Plesset Perturbation Theory

We considered perturbation theory in general in lecture 23. Recall that, given an operator described as

$$\mathbf{A} = \mathbf{A}^{(0)} + \lambda \mathbf{V} \quad (38-2)$$

where $\mathbf{A}^{(0)}$ is an operator for which we can find eigenfunctions, \mathbf{V} is a perturbing operator, and λ is a dimensionless parameter that maps $\mathbf{A}^{(0)}$ into \mathbf{A} as it varies from 0 to 1, we can express improved estimates of the eigenvalues and eigenfunctions of \mathbf{A} using perturbation theory. In particular, we have

$$\langle \Psi_0^{(0)} | \mathbf{V} | \Psi_0^{(0)} \rangle = a_0^{(1)} \quad (38-3)$$

which says that the first order correction to the eigenvalue is the expectation value of the perturbing operator over the unperturbed wave function, and

$$a_0^{(2)} = \sum_{j>0} \frac{|\langle \Psi_j^{(0)} | \mathbf{V} | \Psi_0^{(0)} \rangle|^2}{a_0^{(0)} - a_j^{(0)}} \quad (38-4)$$

which says that the second-order correction also can be computed using only the zeroth-order eigenfunctions and eigenvalues.

So, how can we use this in the case of the Hamiltonian operator? That is, can we somehow pick an $\mathbf{A}^{(0)}$ and a \mathbf{V} that when added together make \mathbf{H} , the proper Hamiltonian, and for which the eigenfunctions of $\mathbf{A}^{(0)}$ are known? In 1934, Møller and Plesset proposed choices for $\mathbf{A}^{(0)}$ and \mathbf{V} with this goal in mind (Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618), and the application of their prescription is now typically referred to by the acronym MP n where n is the order at which the perturbation theory is truncated, e.g., MP2, MP3, etc.

The MP approach takes $\mathbf{A}^{(0)}$ to be the sum of the one-electron Fock operators, i.e., a Hamiltonian that does not account for electron correlation and double counts electron-electron repulsions. Thus

$$\mathbf{A}^{(0)} = \sum_{i=1}^n f_i \quad (38-5)$$

where n is the number of basis functions and f_i is defined in the usual way according to eq. 27-5. In addition, $\Psi^{(0)}$ is taken to be the HF wave function, which is a Slater determinant formed from the occupied orbitals. By analogy to eq. 26-5, it is straightforward to show that the eigenvalue of $\mathbf{A}^{(0)}$ when applied to the HF wave function is the sum of the occupied orbital energies, i.e.,

$$\mathbf{A}^{(0)}\Psi^{(0)} = \sum_i^{\text{occ.}} \epsilon_i \Psi^{(0)} \quad (38-6)$$

where the orbital energies are the usual eigenvalues of the specific one-electron Fock operators. The sum on the r.h.s. thus defines the eigenvalue $a^{(0)}$.

Recall that this is *not* the way the electronic energy is usually calculated in an HF calculation—it is the expectation value for the *correct* Hamiltonian and the HF wave function that determines that energy. The “error” in eq. 38-6 is that each orbital energy includes the repulsion of the occupying electron(s) with all of the other electrons. Thus, each electron-electron repulsion is counted twice (once in each orbital corresponding to each pair of electrons). So, the correction term \mathbf{V} that will return us to the correct Hamiltonian and allow us to use perturbation theory to improve the HF wave function and eigenvalues must be the difference between counting electron repulsion once and counting it twice. Thus,

$$\mathbf{V} = \sum_i^{\text{occ.}} \sum_{j>i}^{\text{occ.}} \frac{1}{r_{ij}} - \sum_i^{\text{occ.}} \sum_j^{\text{occ.}} \left(J_{ij} - \frac{1}{2} K_{ij} \right) \quad (38-7)$$

where the first term on the r.h.s. is the proper way to compute electron repulsion and the second term is how it is computed from summing over the Fock operators for the occupied orbitals where J and K are the Coulomb and exchange operators defined in Lecture 27.

So, let us now consider the first-order correction $a^{(1)}$ to the zeroth-order eigenvalue defined by eq. 38-6. In principle, from eq. 38-3, we operate on the HF wave function $\Psi^{(0)}$ with \mathbf{V} defined in eq. 38-7, multiply on the left by $\Psi^{(0)}$, and integrate. By inspection, cognoscenti should not have much trouble seeing that the result will be the negative of the electron-electron repulsion energy. However, if that is not obvious, there is no need to carry through the integrations in any case. That is because we can write

$$\begin{aligned} a^{(0)} + a^{(1)} &= \langle \Psi^{(0)} | \mathbf{A}^{(0)} | \Psi^{(0)} \rangle + \langle \Psi^{(0)} | \mathbf{V} | \Psi^{(0)} \rangle \\ &= \langle \Psi^{(0)} | \mathbf{A}^{(0)} + \mathbf{V} | \Psi^{(0)} \rangle \\ &= \langle \Psi^{(0)} | \mathbf{H} | \Psi^{(0)} \rangle \\ &= E_{\text{HF}} \end{aligned} \quad (38-8)$$

i.e., the Hartree-Fock energy is the energy correct through first-order in Møller-Plesset perturbation theory. Thus, the second term on the r.h.s. of the first line of eq. 38-8 must indeed be the negative of the overcounted electron-electron repulsion already noted to be implicit in $a^{(0)}$.

As MP1 does not advance us beyond the HF level in determining the energy, we must consider the second-order correction to obtain an estimate of correlation energy. Thus, we must evaluate eq. 38-4 using the set of all possible excited-state eigenfunctions and eigenvalues of the operator $\mathbf{A}^{(0)}$ defined in eq. 38-5. Happily enough, that is a straightforward process, since within a finite basis approximation, the set of all possible excited eigenfunctions is simply all possible ways to distribute the electrons in the HF orbitals, i.e., all possible excited CSFs appearing in eq. 37-6.

Let us consider the numerator of eq. 38-4. Noting that \mathbf{V} is $\mathbf{H}-\mathbf{A}^{(0)}$, we may write

$$\begin{aligned}
 \sum_{j>0} \langle \Psi_j^{(0)} | \mathbf{V} | \Psi_0^{(0)} \rangle &= \sum_{j>0} \langle \Psi_j^{(0)} | \mathbf{H} - \mathbf{A}^{(0)} | \Psi_0^{(0)} \rangle \\
 &= \sum_{j>0} \left[\langle \Psi_j^{(0)} | \mathbf{H} | \Psi_0^{(0)} \rangle - \langle \Psi_j^{(0)} | \mathbf{A}^{(0)} | \Psi_0^{(0)} \rangle \right] \\
 &= \sum_{j>0} \left[\langle \Psi_j^{(0)} | \mathbf{H} | \Psi_0^{(0)} \rangle - \sum_i^{\text{occ.}} \epsilon_i \langle \Psi_j^{(0)} | \Psi_0^{(0)} \rangle \right] \\
 &= \sum_{j>0} \langle \Psi_j^{(0)} | \mathbf{H} | \Psi_0^{(0)} \rangle
 \end{aligned} \tag{38-9}$$

where the simplification of the r.h.s. on proceeding from line 3 to line 4 derives from the orthogonality of the ground and excited-state Slater determinants. As for the remaining integrals, we know from our discussion of CI matrix elements that we need only consider integrals involving doubly excited determinants. So we may simplify eq. 38-9 to

$$\sum_{j>0} \langle \Psi_j^{(0)} | \mathbf{V} | \Psi_0^{(0)} \rangle = \sum_i^{\text{occ.}} \sum_{j>i}^{\text{occ.}} \sum_a^{\text{vir.}} \sum_{b>a}^{\text{vir.}} [(ij|ab) - (ia|jb)] \tag{38-10}$$

where the two electron integrals are those defined by eq. 27-10.

As for the denominator of eq. 38-4, from inspection of eq. 38-6, $a^{(0)}$ for each doubly excited determinant will differ from that for the ground state only by including in the sum the energies of the virtual orbitals into which excitation has occurred and excluding the energies of the two orbitals from which excitation has taken place. Thus, the full expression for the second-order energy correction is

$$a^{(2)} = \sum_i^{\text{occ.}} \sum_{j>i}^{\text{occ.}} \sum_a^{\text{vir.}} \sum_{b>a}^{\text{vir.}} \frac{[(ij|ab) - (ia|jb)]^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \tag{38-11}$$

The sum of the HF energy and $a^{(2)}$ defines the MP2 energy.

MP2 calculations can be done reasonably rapidly because eq. 38-11 can be efficiently evaluated. The scaling behavior of the MP2 method is roughly N^5 , where N is the number of basis functions (note the improvement over CISD). Analytic gradients and second-derivatives are available for this level of theory, too, so it can conveniently be used to explore PESs. Finally, MP2, and indeed all orders of MP n theory, are size-extensive, which is a particularly desirable feature.

However, it should be noted that the Møller-Plesset formalism is potentially rather dangerous in design. Perturbation theory works best when the perturbation is small (because the Taylor expansions in eqs. 23-2 and 23-3 are then expected to be quickly convergent). But, in the case of MP theory, the perturbation is the full electron-electron repulsion energy, which is a rather large contributor to the total energy! So, there is no reason to expect that an MP2 calculation will give a value for the correlation energy that is particularly good. In addition, the MP n methodology is *not* variational. Thus, it is possible that the MP2 estimate for the correlation energy will be too large instead of too small (however, this rarely happens in practice because basis set limitations always introduce error in the direction of underestimating the correlation energy).

Naturally, if one wants to improve convergence, one can proceed to higher orders in perturbation theory (note, however, that even at infinite order, there is no guarantee of convergence when a finite basis set has been used). At 3rd order, it is still true that only matrix elements involving doubly-excited determinants need be evaluated, so MP3 is not too much more expensive than MP2. A fair body of empirical evidence, however, suggests that MP3 calculations tend to offer rather little improvement over MP2. Analytic gradients are not available for 3rd and higher orders of perturbation theory, so optimizing geometries is tedious.

At the MP4 level, integrals involving triply- and quadruply-excited determinants appear. The evaluation of the terms involving triples is the most costly, and scales as N^7 . Empirically, MP4 calculations can be quite good, typically accounting for more than 95% of the correlation energy with a good basis set. However, although ideally the MP n results for any given property would show convergent behavior as a function of n , the more typical observation is oscillatory, and it can be difficult to extrapolate accurately from only four points (MP1=HF, MP2, MP3, MP4). As a rough rule of thumb, to the extent that the results of an MP2 calculation differ from HF, say for the energy difference between two isomers, the difference tends to be overestimated. MP3 usually pushes the result back in the HF direction, by a variable amount. MP4 increases the difference again, but in favorable cases by only a small margin, so that some degree of convergence may be relied upon. An example is shown below for the relative energy of two isomers of H_2CO_2 , a powerful oxidant.

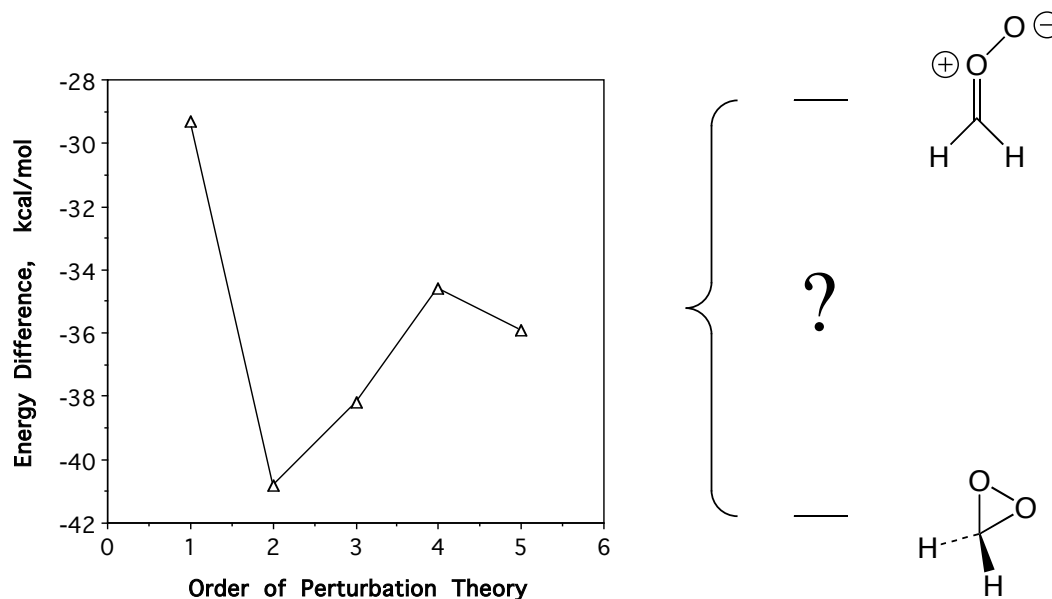


Figure. Slowly oscillatory behavior of MP_n theory for the energy separation between carbonyl oxide and dioxirane. Based on this graph, what would be your best guess for the infinite-order energy separation?

Summary of Correlated Methods

For a typical equilibrium structure, the HF level of theory predicts bond lengths that are usually a bit too short. It is simple to rationalize this using eq. 37-6. To the extent that correlated methods include excited configurations in the wave function expansion, and to the extent that the orbitals into which excitations occur typically have some antibonding character, this tends to increase bond lengths in order to lower the energy. This also explains why HF calculations systematically compute vibrational frequencies to be too high—the bonds have too much bonding character. As a rule, then, the MP2 level is an excellent choice for geometry optimizations of *minima* that include correlation energy, and significant improvements can be obtained at fairly reasonable cost.

A rough quality ordering of the correlated methods we have discussed is

$$\text{HF} < \text{MP2} \sim \text{MP3} < \text{CID} < \text{CISD} \\ < \text{MP4SDQ} < \text{MP4} < \text{MP5} < \text{etc.} \quad (38-12)$$

The below table provides a more quantitative feel for the performance summary embodied in eq. 38-12 using data for the absolute errors in various levels of theory compared to full CI for HB, H₂O, and HF using a basis set having two basis functions per valence orbital, one per core orbital, and one set of functions of one higher angular

momentum than that required for the first-row atoms (i.e., d functions) (Bartlett, R. J. in *Modern Electronic Structure Theory*, D. R. Yarkony, Ed. World Scientific, New York, NY: 1995; Part 2, Chapter 16). In this case, calculations were carried out both at the equilibrium geometries, and also at geometries where the X–H bonds were stretched by 50% and 100%; correlation should become more important in describing these higher energy species. The ordering of the levels in the table is approximately that listed in eq. 38-12. As expected, the lower levels of correlation treatment degrade markedly compared to the higher levels when the bonds are stretched. The scaling behavior of the various methods is also listed as a function of number of basis functions N . The job of the applied quantum chemist in a typical situation is to decide what level of theory provides acceptable accuracy given the inevitable constraint of finite computational resources.

Table. Average errors in correlation energies (kcal mol⁻¹) compared to full CI for various methods applied to HB, H₂O, and HF at both equilibrium and bond-stretched geometries.

Level of Theory	Equilibrium geometry	Eq. and stretched geometries	Scaling behavior
MP2	10.4	17.4	N^5
MP3	5.0	14.4	N^6
CISD	5.8	13.8	N^6
MP4	1.3	3.7	N^7
MP5	0.8	3.2	N^8
MP6	0.3	0.9	N^9

Homework

To be turned in for possible grading May 5:

The only thing left:

let Ψ_{poem} collapse to
a single haiku