

Answers to Homework Set 7

From lecture 25: Using the third root of the secular equation for the allyl system, verify the orbital coefficients given in eq. 25-16

The second root was $E = \alpha$. Plugging that value into the linear equations

$$\sum_{i=1}^N a_i (H_{ki} - ES_{ki}) = 0 \quad \forall k$$

recalling that for the allyl system $H_{11} = H_{22} = H_{33} = \alpha$, $H_{12} = H_{21} = H_{23} = H_{32} = \beta$, $H_{13} = H_{31} = 0$, $S_{11} = S_{22} = S_{33} = 1$, and all other S values are 0, we have

$$a_1 [\alpha - (\alpha - \sqrt{2}\beta) \cdot 1] + a_2 [\beta - (\alpha - \sqrt{2}\beta) \cdot 0] + a_3 [0 - (\alpha - \sqrt{2}\beta) \cdot 0] = 0$$

$$a_1 [\beta - (\alpha - \sqrt{2}\beta) \cdot 0] + a_2 [\alpha - (\alpha - \sqrt{2}\beta) \cdot 1] + a_3 [\beta - (\alpha - \sqrt{2}\beta) \cdot 0] = 0$$

$$a_1 [0 - (\alpha - \sqrt{2}\beta) \cdot 0] + a_2 [\beta - (\alpha - \sqrt{2}\beta) \cdot 0] + a_3 [\alpha - (\alpha - \sqrt{2}\beta) \cdot 1] = 0$$

These equations simplify to

$$a_1 \sqrt{2}\beta + a_2 \beta = 0$$

$$a_1 \beta + a_2 \sqrt{2}\beta + a_3 \beta = 0$$

$$a_2 \beta + a_3 \sqrt{2}\beta = 0$$

If we subtract the third equation from the first, we obtain

$$a_1 \sqrt{2}\beta - a_3 \sqrt{2}\beta = 0$$

which gives

$$a_1 = a_3$$

If we use this relationship in the second equation above we have

$$a_1\beta + a_2\sqrt{2}\beta + a_1\beta = 0$$

which gives

$$a_2 = -\sqrt{2}a_1$$

Normalization requires that

$$\sum_{i=1}^3 |a_i|^2 = 1$$

which leads to the final result

$$a_{13} = \frac{1}{2}, \quad a_{23} = -\frac{\sqrt{2}}{2}, \quad a_{33} = \frac{1}{2}$$

QED.

From lecture 26:

What is the Hartree-product wave function for 2 non-interacting quantum mechanical harmonic oscillators (QMHOs) of reduced mass 1 a.u. in a potential having a force constant of 1 a.u., where the first QMHO is in the ground state and the second is in the first excited state? Determine the energy of the two QMHO system as an expectation value of the Hartree-product wave function. Is the correct Hamiltonian for this system separable into one-QMHO terms? If the QMHOs *were* interacting, explain how you could use perturbation theory to determine the energy of the system correct to first order (you don't have to actually do it, just explain *how* to do it).

The Hartree product is simply the product of the 2 relevant QMHO wave functions. Thus it will be (in a.u.)

$$\begin{aligned}\Psi_{\text{HP}}(x_1, x_2) &= \left(\frac{1}{\pi}\right)^{1/4} e^{-x_1^2/2} \left(\frac{1}{4\pi}\right)^{1/4} 2x_2 e^{-x_2^2/2} \\ &= \left(\frac{2}{\pi}\right)^{1/2} e^{-x_1^2/2} x_2 e^{-x_2^2/2}\end{aligned}$$

where each QMHO has its own x coordinate describing its position in the box.

Since the QMHOs are defined to be non-interacting, the total Hamiltonian is indeed separable as simply the sum of the Hamiltonian operators for each QMHO. In that case, the Hartree-product wave function is an eigenfunction of the Hamiltonian and its eigenvalue is the sum of the one-particle eigenvalues. Thus the energy for this system is (in a.u., see eq. 9-22)

$$\begin{aligned}E &= \frac{1}{2} + \frac{3}{2} \\ &= 2\end{aligned}$$

If the particles *were* interacting, then the total Hamiltonian would be

$$H = \sum_{i=1}^2 \left(-\frac{1}{2} \frac{d^2}{dx_i^2} + \frac{1}{2} kx_i^2 \right) + V'$$

where V' would describe the interaction, e.g.,

$$V' = \frac{1}{|x_1 - x_2|}$$

The first-order correction to the energy for the *unperturbed* Hamiltonian is determined as

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

so we would need to evaluate

$$\frac{2}{\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{e^{-x_1^2/2} x_2 e^{-x_2^2/2}}{|x_1 - x_2|} dx_1 dx_2$$

which doesn't look as though it would be so pleasant, but that's how one would do it...

From lecture 27:

None assigned.

From lecture 28:

Consider the phosphine molecule (PH_3). If we decide to do a calculation on phosphine and use the STO-3G basis set, how many contracted basis functions will we need in order to minimally represent the total number of atomic orbitals spanned by the core and valence electrons of the phosphorus atom and the three hydrogen atoms? How many one-electron integrals will there be that require evaluation? How many two-electron integrals will require evaluation? In each of the last two cases, how many *primitive* integrals will need to be evaluated? Do you see anything that makes the workload slightly less onerous than your formal analysis? How many occupied orbitals will there be in the final Slater determinant?

Phosphorus requires 1s, 2s, 2p, 3s, and 3p orbitals (the 3d orbitals are not occupied so we do not need them in a minimal representation). The total basis functions on P are thus $1 + 1 + 3 + 1 + 3 = 9$. There are 3 H atoms, each of which requires one 1s function, so the grand total number of basis functions N is 12. There are N^2 kinetic-energy one-electron integrals and MN^2 nuclear-attraction integrals where M is the number of nuclei, i.e., 4. So, that's 144 in the first case and 576 in the second case for a total of 720 one-electron integrals. There are formally N^4 2-electron integrals, which is 20,736.

The numbers computed above involve the contracted basis functions, each of which, since the basis is STO-3G, is composed of 3 primitive functions. Thus, for any individual one-electron integral, there will be $3 \times 3 = 9$ separate integrals involving the primitives. There are thus $9 \times 720 = 6480$ individual primitive one-electron integrals. As for the two-electron integrals, again, every individual integral will require considering every possible combination of constituent primitives which is $3 \times 3 \times 3 \times 3 = 81$. Thus, the total number of primitive two-electron integrals is $81 \times 20,736 = 1,679,616$. Symmetry reduces these numbers as described in Lecture 29 by a fairly substantial margin. The final Slater determinant will require $n/2$ doubly occupied molecular orbitals to hold the n electrons of phosphine. Given the molecular formula, that is 15 electrons from P plus 3 from three H atoms for a total of 18 electrons and thus a Slater determinant comprised of 9 MOs.

or (since there was an error in the original homework that referred to "phosphine (HCl)")

Consider the hydrogen chloride molecule (HCl). If we decide to do a calculation on HCl and use the STO-3G basis set, how many contracted basis functions will we need in order to minimally represent the total number of atomic orbitals spanned by the core

and valence electrons of the chlorine atom and the hydrogen atom? How many one-electron integrals will there be that require evaluation? How many two-electron integrals will require evaluation? In each of the last two cases, how many primitive integrals will need to be evaluated? Do you see anything that makes the workload slightly less onerous than your formal analysis? How many occupied orbitals will there be in the final Slater determinant?

Chlorine requires 1s, 2s, 2p, 3s, and 3p orbitals (the 3d orbitals are not occupied so we do not need them in a minimal representation). The total basis functions on Cl are thus $1 + 1 + 3 + 1 + 3 = 9$. There is 1 H atom, which requires one 1s function, so the grand total number of basis functions N is 10. There are N^2 kinetic-energy one-electron integrals and MN^2 nuclear-attraction integrals where M is the number of nuclei, i.e., 2. So, that's 100 in the first case and 200 in the second case for a total of 300 one-electron integrals. There are formally N^4 2-electron integrals, which is 10,000.

The numbers computed above involve the contracted basis functions, each of which, since the basis is STO-3G, is composed of 3 primitive functions. Thus, for any individual one-electron integral, there will be $3 \times 3 = 9$ separate integrals involving the primitives. There are thus $9 \times 300 = 2700$ individual primitive one-electron integrals. As for the two-electron integrals, again, every individual integral will require considering every possible combination of constituent primitives which is $3 \times 3 \times 3 \times 3 = 81$. Thus, the total number of primitive two-electron integrals is $81 \times 10,000 = 810,000$. Symmetry reduces these numbers as described in Lecture 29 by a fairly substantial margin. The final Slater determinant will require $n/2$ doubly occupied molecular orbitals to hold the n electrons of hydrogen chloride. Given the molecular formula, that is 17 electrons from Cl plus 1 from the H atom for a total of 18 electrons and thus a Slater determinant comprised of 9 MOs.