

Test exam in TKJ4170

Quantum Chemistry

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Introduction:

Originally the course, TKJ4170: Quantum Chemistry, was intended to have a report of a computational exercise. Because of the Covid-19 virus ravaging the world in this university semester, this report has been replaced by a test-exam specially designed by the course lecturer. The following text is an answer to the questions posed on the test-exam.

Problem 1:

In quantum chemistry we solve eigenvalue problems to determine the electronic energy levels of molecules. This was done in a computational exercise in this course as well (as previously mentioned). Three different methods were used Hartree-Fock (abbreviated as HF) and two versions of Coupled Cluster (CC), to be elaborated more on later. These methods are used rather than just solving the time-independent Schrodinger equation given as

$$H \psi = E \psi \quad (1)$$

Where H = Hamiltonian, E = Energy and ψ = wave-function. Due to the matrices being very large and we need approximations run of very big computers to solve them (which is why we used the Idun cluster computer network to do the computational exercise). Equation (1) can basically only be solved for very simple systems.

If one solves (1) then one can find all the quantum mechanical information one wants about a system. The wave-function in that equation represents basically the atomic orbital. In the orbital there is a high probability of finding an electron. The expectation value is given as:

$$E_0 = \langle \psi * |H|\psi \rangle \quad (2)$$

This is relevant for us due to the variation principle theorem. The theorem states that if a normalized wavefunction satisfies the normalized boundary condition, then the expectation value of the Hamiltonian is an upper bound to the ground state energy. Meaning that when $\psi * \psi = 1$, then we have that $\langle \psi * |H|\psi \rangle \geq E_0$. From this we understand that the expectation value gives us the ground state energy. From my previous studies on quantum computers I can make a comparison to a phenomenon I witness at that field. Meaning that this is reminiscent of the optimization condition where one is interested to find the global minimum of a function.

Now to actually discuss the choices of methods. HF is perhaps the most basic of them. It is done without using experimental data. We write the basic algorithm as:

$$f \psi_a = E_a \psi_a \quad (3)$$

Where f in (3) is the fock operator, and the rest are as usual (wavefunctions and energy). This approximation is the molecular orbital approximation meaning the approximation for that there are electrons occupying that particular orbital. From Trygve Helgaker's lecture on high-accuracy quantum chemistry we have the following properties of the method (widely used as a basis for other methods it must be said):

- It is the best single-determinantal approximation to the exact wave-function
- Each electron moves in the mean field of all other electrons
- It provides an uncorrelated description: meaning average rather than instant interactions (will be explained more later)
- Typical errors are 0.5 percent in energy

We see here that it does not take into account something called electron correlation. An improved description would describe the effects of electron correlation. This is because in real space the electrons often experience collisions, in fact we have a term for it in semiconductor and solid state physics, the electrons mean free path (important parameter). In orbitals this is represented by excitations from occupied to virtual spin orbitals (like double excitations).

Therefore, we go over to using coupled cluster method for improvement in our model. The CC state is obtained from the HF by applying all possible excitation operators. In equation (4) I will use the notation Trygve Helgaker uses in his presentation to exemplify this:

$$|CC\rangle = (1 + t_i^a X_i^a) \dots (1 + t_{ij}^{ij} X_{ij}^{ij}) \dots (1 + t_{ijk}^{ijk} X_{ijk}^{ijk}) \dots |HF\rangle \quad (4)$$

CCS is the single excitation, meaning the first expression (with the probability amplitude). CCSD is the double excitation (n^6). Here the computational scaling is represented as n = number of orbitals and the power of it is the excitation level, but with a small caveat. The scaling is $O(n^{2m+2})$, so the excitation is $m = 2$.

Problem 2:

The question asks us to discuss what it means that we've done all the calculations for a closed-shell state. This should be done in terms of eigenvalues of the spin angular momentum operators S^2 and S_z .

With a closed shell we mean a configuration where the valence shell is completely filled. A configuration that we consider to be stable. The best example of this is the noble gas configuration seen in the Periodic table. Basically when we fill a shell, the resulting electron distribution becomes spherically symmetrical because of:

$$\sum_{m=-l}^l |Y_{lm}(\theta, \phi)|^2 = \frac{2l+1}{4\pi}$$

From this the quantum numbers of the closed shell are easily determined because there is only one possible state representing a closed shell giving us the following quantum numbers:

$$s = 0$$

$$l = 0$$

$$j = 0$$

We here have a small s and a big S in the text of the assignment. It should here be said that the big S denotes the angular momenta of a collection of particles. But we know that since there is a closed shell state, then $S = 0$ further leading us to only have one possible value of S_z , i.e. $S_z = 0$. This is the coupled picture.

Second part of the question wanted us to look at this from the allowed values of the eigenvalues perspective. Here we've shown that the total angular momentum $j = 0$. So, what are the allowed eigenvalues for the spin angular momentum? From $S = 0$ we understand that we must have electrons in the shell that are anti-parallel denoted as either $\uparrow\downarrow$ or $\downarrow\uparrow$. The possible values of $S^2 = (S_1 + S_2)^2$ are $\hbar^2 s(s+1)$. Here s can be 0 or 1. We already know that since it is a closed shell that $s = 0$. That gives us an allowed eigenvalue of 0. We also look at an orbital with two electrons and closed shell. We then get the eigenstates in arrow notation

and s in the table below.

Eigenstates	m_1	m_2	s
$ \uparrow_1\uparrow_2\rangle$	$\frac{1}{2}$	$\frac{1}{2}$	1
$ \uparrow_1\downarrow_2\rangle$	$\frac{1}{2}$	$-\frac{1}{2}$	0
$ \downarrow_1\uparrow_2\rangle$	$-\frac{1}{2}$	$\frac{1}{2}$	0
$ \downarrow_1\downarrow_2\rangle$	$-\frac{1}{2}$	$-\frac{1}{2}$	-1

We then have four spins we can insert in the equation for the eigenvalues above. But Pauli's rule and the fact that $S^2 = 0$, only allow the anti-parallel eigenstates thereby giving us the eigenstates of 0.

Excited states occur if there is an external source like electromagnetic source or thermic source. The photoelectric effect is a good example. An excited configuration for a closed shell gives us two states $2S + 1 = 0$ and $2S + 1 = 3$ with $S = -1/2$ (singlet) and $S = 1$ (triplet). The z-components of the angular momentum for 2 electrons can add to give +1, 0 or -1 units of \hbar .

We then have new eigenvalues based on the table and the equation given earlier in the answer. $\uparrow\uparrow$ gives an eigenvalue of $2\hbar$ and $\downarrow\downarrow$ gives an eigenvalue of 0 because the value inserted in the eigenvalue equation comes from the value obtained because of addition from the z-components. The triplet can also be combination of the different arrow notation (or eigenstates) in the table, but the eigenvalue is still $2\hbar$ since $s = 1$.

Problem 3:

Problem 3 says that we should discuss how time-independent non-degenerate perturbation theory is used in quantum chemistry. Perturbation has a slightly different meaning in mathematics (primarily from group theory) and quantum mechanics. In this context we

consider perturbation to be a Hamiltonian of a system that differs by a contribution that is independent of time. As exemplified by the equation (5).

$$H = H^0 + H^1 \quad (5)$$

Where H^1 is the perturbation.

In the curriculum we are presented with two systems: the two-level system and the many-level system. We take a look at the first system. In equation (1) we have the following solution for the unperturbed system:

$$\psi = c_1 \psi_1^0 + c_2 \psi_2^0 \quad (6)$$

This equation (6) is inserted into (1) and we get:

$$c_1 (H - E)|1\rangle + c_2 (H - E)|2\rangle = 0 \quad (7)$$

By multiplying from left by the bras $\langle 1|$ and $\langle 2|$ in turn we get the following expression:

$$c_1 (H_{11} - E) + c_2 H_{12} = 0 \quad (8)$$

$$c_1 H_{21} + c_2 (H_{22} - E) = 0 \quad (9)$$

The perturbed wavefunction will be written as:

$$\psi_0 + \psi_0^0 + \lambda \psi_0^1 + \lambda^2 \psi_0^2 + \dots \quad (10)$$

Likewise the perturbed will be written as in equation (11):

$$E_0 = E_0^0 + \lambda E_0^1 + \lambda^2 E_0^2 + \dots \quad (11)$$

The wavefunction gives us the orbital, and the energy gives us the discrete energy levels electrons can be in.

MP2 stands for the Møller-Plesset perturbation theory and is a widely used method for approximating the correlation energy of the molecules. We've already seen how the energy and wavefunction have been expanded above. Substituting these into (1) gives us:

$$H_0 \psi_0 = E^0 \psi_0$$

$$H_0 \psi^1 + V \psi_0 = E^0 \psi^1 + E^1 \psi_0$$

$$H_0 \psi^2 + V\psi^1 = E^0\psi^2 + E^1\psi^1 + E^2\psi_0$$

Multiplying each of the equations with ψ_0 and integrating gives us:

$$E^0 = \langle \psi_0 | H_0 | \psi_0 \rangle$$

$$E^1 = \langle \psi_0 | V | \psi_0 \rangle$$

$$E^2 = \langle \psi_0 | V | \psi_1 \rangle$$

And thereby becoming:

$$E_0 = \langle \psi_0 | H_0 + V | \psi_0 \rangle$$

Leading us to $E_0 = E^0 + E^1$ and the correlation energy is then:

$$E_{corr} = E_0^2 + E_0^3 + E_0^4 + \dots$$

This is in essence the MP2 perturbation method.