Queen Mary
University of London

M. Sci./M. Sc. Examination by Course Unit

Thursday 1$^{st}$ May 2014 14:30–17:00

**PHY7016U/P** **Electronic Structure Methods** Duration: 2 hours 30 minutes

You are not permitted to read the contents of this question paper until instructed to do so by an invigilator.

## Instructions:

This paper contains five questions. **Answer any three questions**.
If you answer more questions than specified, only the *first* answers (up to the specified number) will be marked. Cross out any answers that you do not wish to be marked.

Only non-programmable calculators are permitted in this examination. Please state on your answer book the name and type of machine used.

Complete all rough working in the answer book and cross through any work which is not to be assessed.

**Important note:** The *Academic Regulations* state that possession of unauthorised material at any time when a student is under examination conditions is an assessment offence and can lead to expulsion from QMUL.

Please check now to ensure you do not have any notes, mobile phones or unathorised electronic devices on your person. If you have any then please raise your hand and give them to an invigilator immediately. Please be aware that if you are found to have hidden unauthorised material elsewhere, including toilets and cloakrooms, it will be treated as being found in your possession. Unauthorised material found on your mobile phone or other electronic device will be considered the same as being in possession of paper notes. A mobile phone that causes a disruption is also an assessment offence.

**Exam papers must not be removed from the exam room.**

Examiners: Dr A. J. Misquitta & Prof. M. T. Dove

© Queen Mary University of London (2014)

**Question 1**

(a) Using the variational principle, prove that a linear expansion of the form

$$|C\rangle = \sum_{i=1}^{m} c_i |i\rangle$$

where the $|i\rangle$ are a set of non-orthogonal basis functions, can be optimized to lead to the following set of linear equations:

$$\mathbf{Hc} = E(\mathbf{c})\mathbf{Sc},$$

where $H_{ij} = \langle i|H|j\rangle$ and $S_{ij} = \langle i|j\rangle$. Under what condition does this set of linear equations have non-trivial solutions? **[5 marks]**

(b) The Schrödinger equation (in atomic units) for a hydrogen atom in a uniform electric field $F$ in the $z$ direction is

$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r} + Fr\cos(\theta)\right)|\phi\rangle = (H_0 + Fr\cos(\theta))|\phi\rangle = E(F)|\phi\rangle.$$

Use the trial wavefunction $|\tilde{\phi}\rangle = c_1|1s\rangle + c_2|2p_z\rangle$ where $|1s\rangle$ and $|2p_z\rangle$ are normalized eigenfunctions of $H_0$:

$$|1s\rangle = \sqrt{\frac{1}{\pi}}e^{-r}$$

$$|2p_z\rangle = \sqrt{\frac{1}{32\pi}}re^{-r/2}\cos(\theta),$$

to find an upper bound to E(F).

You may wish to use

$$\int_0^\infty r^n e^{-r/a} dr = a^{n+1}\Gamma(n+1).$$

**[15 marks]**

(c) Assuming the field $F$ is sufficiently small, expand the ground state in powers of $F$. Compare this with $E(F) = E(0) - \frac{1}{2}\alpha F^2 + \cdots$ to identify the polarizability $\alpha$. The exact value of this polarizability if 4.5 a.u. Can we improve the variational expansion by including the $|2p_x\rangle$ and $|2p_y\rangle$ states? Justify your answer. **[5 marks]**

## Question 2

(a) The Hellmann–Feynman theorem states that for an exact eigenstate $|\psi\rangle$, the first-order change in the energy due to a perturbation may be calculated as the expectation value of the perturbation operator. That is, if $H(\alpha) = H + \alpha V$ and if $H(\alpha)|\psi_\alpha\rangle = E(\alpha)|\psi_\alpha\rangle$, then

$$\left.\frac{\partial E(\alpha)}{\partial \alpha}\right|_{\alpha=0} = \langle\psi|V|\psi\rangle.$$

Prove that this theorem also holds for variational wavefunctions of the form $\tilde{\psi} = \tilde{\psi}(c_1, c_2, \cdots, c_n)$ where $c_i$ are variational parameters. **[15 marks]**

(b) Now consider a Hamiltonian of the form

$$H(\mathbf{R}_I) = -\frac{1}{2}\sum_i \nabla_i^2 + \sum_{j>i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \sum_{J>I} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$

(i) By considering a Hamiltonian with displaced nuclear coordinates $H(\mathbf{R}_I + \alpha_I)$ use the Hellmann–Feynman theorem to derive an expression for the forces on the nuclei.

(ii) Comment on the applicability of this expression for a variational wavefunction with basis functions that are centered on the nuclei.

**[10 marks]**

## Question 3

(a) Consider a minimal-basis description of the $H_2$ molecule using as basis functions the $1\mathbf{s_A}(\mathbf{r})$ and $1\mathbf{s_B}(\mathbf{r})$ atomic orbitals of the interacting atoms located at positions **A** and **B**. Here $1\mathbf{s_A}(\mathbf{r}) = \pi^{-1/2}\exp(-r_A)$ and $1\mathbf{s_B}(\mathbf{r}) = \pi^{-1/2}\exp(-r_B)$, where $r_A = |\mathbf{r} - \mathbf{A}|$ and $r_B = |\mathbf{r} - \mathbf{B}|$.

- (i) Construct normalized symmetry-adapted atomic orbitals for $H_2$ and sketch them.
- (ii) Use these orbitals to construct all possible 2-electron molecular wavefunctions for $H_2$. Label these 2-electron wavefunctions according to whether they are of *gerade* or *ungerade* symmetry. Which of these is the restricted Hartree–Fock (RHF) spin singlet ground state wavefunction?
- (iii) The energy of a single determinant 2-electron state $|\Psi\rangle = |\chi_1\chi_2\rangle \equiv |12\rangle$ is given by

$$E = \langle\Psi|H|\Psi\rangle = \langle 1|h|1\rangle + \langle 2|h|2\rangle + \langle 12|12\rangle - \langle 12|21\rangle.$$

  where $h$ is the one-electron Hamiltonian and $\langle ij|kl\rangle$ are two-electron integrals. Use this result to work out the energy of the RHF ground-state wavefunction for $H_2$.
- (iv) Derive the dissociation limit of this energy.

**[10 marks]**

(b) The configuration interaction (CI) wavefunction for $H_2$ takes the form

$$|{}^1\Sigma_g^+(\tau)\rangle = \cos(\tau)|1\sigma_{\rm g}^2\rangle + \sin(\tau)|1\sigma_{\rm u}^2\rangle,$$

where $\tau$ is a variational parameter.

- (i) Explain why only these two configurations can mix.
- (ii) Determine the energy of the CI state and, using the variational principle, determine the value of $\tau$ at which this energy attains its extrema.
- (iii) Show that, in the dissociation limit, the ground state of the CI wavefunction is found using $\tau_0 = -\pi/4$, hence find the corresponding energy.
- (iv) By expressing this energy in the basis of $1\mathbf{s_A}(\mathbf{r})$ and $1\mathbf{s_B}(\mathbf{r})$ show that the CI energy correctly dissociates into the energy of two isolated hydrogen atoms.

**[15 marks]**

**Question 4**

(a) Under uniform scaling of the electronic coordinates $\mathbf{r}_i \rightarrow \alpha\mathbf{r}_i$ we have, for the $N$-electron wavefunction $\Psi(\mathbf{r}_i)$:

$$\Psi(\mathbf{r}_i) \rightarrow \Psi_\alpha(\mathbf{r}_i) = \alpha^{3N/2}\Psi(\alpha\mathbf{r}_i).$$

(i) If $\hat{V}_{\rm ee} = +\sum_{i>j} r_{ij}^{-1}$ is the electron–electron interaction operator and $V_{\rm ee}[\Psi] = \langle\Psi|\hat{V}_{\rm ee}|\Psi\rangle$ show that $V_{\rm ee}[\Psi_\alpha] = \alpha V_{\rm ee}[\Psi]$.

(ii) Show that $\rho_\alpha(\mathbf{r}) = \alpha^3\rho(\alpha\mathbf{r})$.

**[5 marks]**

(b) The scaling relation derived above also holds for density functionals. Consequently we can write it as $V_{\rm ee}[\rho_\alpha] = \alpha V_{\rm ee}[\rho]$. Since the exchange energy functional $E_x[\rho]$ is part of $V_{\rm ee}[\rho]$ it must also satisfy a similar scaling relation, that is, $E_x[\rho_\alpha] = \alpha E_x[\rho]$.

(i) Assuming that $E_x[\rho]$ is a local functional of the density, that is

$$E_x[\rho] = \int k(\rho(\mathbf{r}))d\mathbf{r},$$

where $k(\rho)$ is a function of $\rho$, use the scaling relation to show that $k(\rho) = -C_x\rho^{4/3}$, where $C_x$ is a positive constant. This is called the Slater exchange functional. Why do we define $k(\rho)$ to be negative?

(ii) Hence derive the Slater exchange *potential* $v_x(\mathbf{r})$.

(iii) The asymptotic form of the density of a finite system is $\rho \rightarrow e^{-\beta r}$, where $\beta$ is a constant. Use this result to show that in the (local) Slater approximation, $v_x(\mathbf{r})$ decays exponentially with distance.

**[10 marks]**

(c) (i) Use an asymptotic analysis to show that the exact asymptotic form of the Kohn–Sham exchange-correlation potential is $v_{\rm xc} \rightarrow -1/r$.

(ii) The correlation potential $v_{\rm c}$ is known to be short-ranged, hence the above asymptotic form results from the exchange potential. I.e., $v_{\rm x} \rightarrow -1/r$. Use this result and the one derived in the previous part to show that local exchange density functionals such as the Slater functional will contain a *self interaction* error. Explain in detail the nature of this error and its consequences.

(iii) How might we correct the self-interaction error? Briefly describe possible techniques and their shortcomings.

**[10 marks]**

## Question 5

A semi-classical model for the dispersion (or van der Waals) interaction between two atoms is the coupled Drude oscillator system. Here, we model each atom as a harmonic oscillator with a central, fixed, positive charge $Q$ about which a negative charge $-Q$ oscillates on a spring with spring constant $k$. The Hamiltonian for one such Drude atom is

$$H(\text{osc}) = -\frac{\hbar^2}{2m}\nabla^2 + \frac{1}{2}kr^2,$$

where $\mathbf{r} = (x, y, z)$ is the distance vector of charge $-Q$ from the fixed nucleus. In this picture, a diatomic system is modelled with the Hamiltonian

$$H = H_a + H_b + V,$$

where $H_a$ and $H_b$ are the Drude oscillators of the form $H(\text{osc})$ and separated by distance $R$, and $V$ is the dipole–dipole interaction term given by

$$V = -\frac{Q^2}{4\pi\epsilon_0 R^3}(2z_a z_b - x_a x_b - y_a y_b).$$

(a) (i) Use separation of variables to show that the Hamiltonian $H$ can be split into contributions from the $x$, $y$ and $z$ coordinates and hence find the eigenvalues of this coupled oscillator system. Identify the ground state energy of this system.

(ii) The dispersion energy is defined as the energy of stabilization due to the correlation of dipolar fluctuations that arises from the interaction operator $V$. Expand the ground state energy of the coupled system and show that the leading order energy of stabilization decays as $-C_6/R^6$. What is the coefficient $C_6$?

**[15 marks]**

(b) By relating the charge $Q$ and spring constant $k$ to the atomic polarizability $\alpha$ and by setting $\hbar\omega = E_I$, the atomic ionization energy, show that $C_6$ can be written in terms of physically relevant parameters.

**[5 marks]**

(c) Using the above model for the dispersion interaction, explain why local and semi-local density functionals are unable to describe this interaction at long-range. State a possible way in which this deficiency of local and semi-local density functionals can be fixed. What are the limitations (if any) of this fix.

**[5 marks]**

---

**End of questions**

**An appendix of one page follows**

# Appendix: physical constants

| | |
|---|---|
| Speed of light in vacuum | $c = 2.9979 \times 10^{8}\ \mathrm{m\ s^{-1}}$ |
| Permittivity of free space | $\epsilon_0 = 8.854 \times 10^{-12}\ \mathrm{F\ m^{-1}}$ |
| Permeability of free space | $\mu_0 = 4\pi \times 10^{-7}\ \mathrm{H\ m^{-1}}$ |
| Electronic charge | $e = 1.6022 \times 10^{-19}\ \mathrm{C}$ |
| Planck constant | $h = 6.626 \times 10^{-34}\ \mathrm{J\ s}$ |
| | $\hbar = h/2\pi = 1.055 \times 10^{-34}\ \mathrm{J\ s}$ |
| Boltzmann constant | $k_\mathrm{B} = 1.3807 \times 10^{-23}\ \mathrm{J\ K^{-1}}$ |
| Electron mass | $m = 9.109 \times 10^{-31}\ \mathrm{kg}$ |
| Avogadro number | $N_\mathrm{A} = 6.022 \times 10^{23}\ \mathrm{mol^{-1}}$ |
| Bohr magneton | $\mu_\mathrm{B} = 9.274 \times 10^{-24}\ \mathrm{A\ m^{2}}\quad (\mathrm{or\ J\,T^{-1}})$ |