Queen Mary
University of London

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

3rd May 2016 10:00–12:30

SPA7008U-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

Question 1

In Kohn–Sham density-functional theory, the single-particle equations are of the form

$$\left(-\frac{1}{2}\nabla^2 + v_{\rm S}(\mathbf{r})\right)\chi_i = \epsilon_i \chi_i,$$

where, for an atom, the effective potential is defined as

$$\begin{aligned} v_{\rm S}(\mathbf{r}) &= v_{\rm J}(\mathbf{r}) + v_{\rm ext}(\mathbf{r}) + v_{\rm xc}(\mathbf{r}) \\ &= \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' - \frac{Z}{|\mathbf{r}-\mathbf{R}|} + \frac{\delta E_{\rm xc}[\rho]}{\delta\rho(\mathbf{r})}. \end{aligned}$$

(a) Show that the exact exchange-correlation potential for a neutral atom behaves as $v_{\rm xc} \to -1/r$ as $r \to \infty$. **[7 marks]**

(b) The exchange-correlation potential for the LB94 density functional is defined as

$$v_{\rm xc}^{\rm LB94}(\mathbf{r}) = -\beta n^{1/3}(\mathbf{r}) \frac{x^2}{1 + 3\beta x \sinh^{-1}(x)},$$

where $\beta = 0.05$, $n(\mathbf{r})$ is the electronic density, and the reduced-gradient is defined as $x = |\nabla n|/n^{4/3}$. As $r \to \infty$, $n \to e^{-\alpha r}$, where α is a constant. Show that in this limit $v_{\rm xc}^{\rm LB94} \to -1/r$.

You may find one or both of these results useful:

$$\begin{aligned} &\sinh^{-1}(x) \to x \quad \text{as} \quad x \to 0. \\ &\sinh^{-1}(x) \to -\ln(x^{-1}) \quad \text{as} \quad x \to \infty. \end{aligned}$$

[10 marks]

(c) The exchange-correlation potential from local and semi-local functionals does not possess the $-1/r$ long-range behaviour, but decays to zero exponentially with r. What are the consequences of this on excitation energies?

Using a diagram, explain how the LB94 functional may be used to asymptotically correct local and semi-local functionals.

[8 marks]

Question 2

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

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

where $|\psi\rangle = |\psi_{\alpha=0}\rangle$.

(a) Prove this theorem. **[7 marks]**

(b) Show 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. **[10 marks]**

(c) Demonstrate how this theorem may be used to evaluate molecular properties such as the dipole moment μ_z through the method of finite differences. Explain how such a calculation might be performed in practice. **[8 marks]**

Question 3

(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 orthonormal basis functions, can be optimized to lead to the following set of linear equations:

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

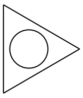
where $H_{ij} = \langle i|H|j\rangle$. Under what condition does this set of linear equations have non-trivial solutions? **[8 marks]**

(b) In the Hückel approximation with a single basis function $|i\rangle$ per atomic site, the Hamiltonian matrix is defined as

$$H_{ij} = \begin{cases} \alpha & \text{if } i = j, \\ \beta & \text{if } i \text{ and } j \text{ neighbours,} \\ 0 & \text{otherwise.} \end{cases}$$

(i) For which class of systems is the approximation valid, and why? What are the physical effects that this approximation is able to account for? **[4 marks]**

(ii) Consider the cyclopropenyl cation $(C_3H_3)^+$ which is the simplest example of an aromatic molecule. This cation has a carbon backbone that may be represented as



Taking the p_z orbitals of the three carbon atoms as your basis (here z is normal to the plane of the carbon ring), solve the secular equations in the Hückel approximation to find the energy eigenvalues. Represent these energy levels diagrammatically and indicate the ground state electron occupancy. **[8 marks]**

(iii) Solve for the normalized molecular orbital coefficients of the lowest energy state and sketch this state. **[5 marks]**

Question 4

(a) Define what is meant by the electron correlation energy E_{corr}. Explain why it is expected to have a negative sign. For which class of systems will $E_{\text{corr}} = 0$? Explain why this will be the case.

[5 marks]

(b) The configuration interaction (CI) wavefunction in intermediate normalised form may be written as

$$|\Psi\rangle = |\Psi_0\rangle + \sum_{ia} c_i^a |\Psi_i^a\rangle + \sum_{i<j,a<b} c_{ij}^{ab} |\Psi_{ij}^{ab}\rangle + \cdots ,$$

where $|\Psi_0\rangle$ is the Hartree–Fock wavefunction to which is included a linear combination of excited-state determinants.

(i) Show that the correlation energy for the CI expansion may be written as

$$E_{\text{corr}} = \langle \Psi_0 | (H - E_0) | \Psi \rangle = \sum_{i<j,a<b} c_{ij}^{ab} \langle \Psi_0 | H | \Psi_{ij}^{ab} \rangle ,$$

where E_0 is the HF energy.

(ii) This expression depends on the CI expansion coefficients for the doubly excited determinants only. Does this imply that the other determinants are not needed? Explain.

[10 marks]

(c) A method is said to be size-extensive if for a system containing non-interacting subsystems, the total energy is equal to the sum of energies of the individual subsystems.

(i) Explain why a truncated CI expansion such as CID (CI with double excitations only) is not size-extensive.

(ii) Hence explain how this problem is alleviated using a coupled-cluster model such as CCD (coupled-cluster with doubles).

[10 marks]

Question 5

In Kohn–Sham density-functional theory, the single-particle equations are of the form

$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{S}}(\mathbf{r})\right)\chi_i = \epsilon_i\chi_i,$$

where the effective potential is defined as

$$\begin{aligned} v_{\mathrm{S}}(\mathbf{r}) &= v_{\mathrm{J}}(\mathbf{r}) + v_{\mathrm{ext}}(\mathbf{r}) + v_{\mathrm{xc}}(\mathbf{r}) \\ &= \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' - \sum_{\alpha}\frac{Z_\alpha}{|\mathbf{r}-\mathbf{R}_\alpha|} + \frac{\delta E_{\mathrm{xc}}[\rho]}{\delta\rho}. \end{aligned}$$

(a) Show that for the hydrogen atom $v_{\mathrm{xc}}(\mathbf{r}) = -v_{\mathrm{J}}(\mathbf{r})$. Hence find the large r behaviour of $v_{\mathrm{xc}}(\mathbf{r})$. **[5 marks]**

(b) The Slater exchange functional is defined as

$$E_x[\rho] = -C_x\int \rho^{4/3}(\mathbf{r})d\mathbf{r},$$

where C_x is a positive constant. Explain why $E_x[\rho]$ is defined to be negative and derive the corresponding exchange potential $v_{\mathrm{X}}(\mathbf{r})$ in this approximation. **[5 marks]**

(c) Use these two results 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 on the energetics (ground state and excited state energies) of the system and on properties such as the polarizability. **[8 marks]**

(d) Explain in detail how this error is reduced in hybrid functionals such as PBE0 which include a fraction of Hartree–Fock exchange. And explain how this error is potentially removed in range-separated functionals. **[7 marks]**

End of questions

An appendix of two pages follows

Appendix: Slater–Condon Rules

$$\begin{aligned}
\mathcal{O}_1 &= \sum_i h(i) \\
\mathcal{O}_2 &= \sum_{i>j} r_{ij}^{-1} \\
H &= \mathcal{O}_1 + \mathcal{O}_2 \\
\langle\Psi|\mathcal{O}_1|\Psi\rangle &= \sum_i h_{ii} \\
\langle\Psi|\mathcal{O}_2|\Psi\rangle &= \sum_{i>j}[\langle ij|ij\rangle - \langle ij|ji\rangle] \\
\langle\Psi|H|\Psi\rangle &= \sum_i \langle i|h|i\rangle + \sum_{i>j}[\langle ij|ij\rangle - \langle ij|ji\rangle] \\
\langle\Psi_i^a|\mathcal{O}_1|\Psi\rangle &= \langle a|h|i\rangle = h_{ai} \\
\langle\Psi_i^a|\mathcal{O}_2|\Psi\rangle &= \sum_j[\langle aj|ij\rangle - \langle aj|ji\rangle] \\
\langle\Psi_i^a|H|\Psi\rangle &= \langle a|h|i\rangle + \sum_j[\langle aj|ij\rangle - \langle aj|ji\rangle] \\
\langle\Psi_{ij}^{ab}|\mathcal{O}_2|\Psi\rangle &= \langle ab|ij\rangle - \langle ab|ji\rangle \\
\langle\Psi_{ij}^{ab}|H|\Psi\rangle &= \langle ab|ij\rangle - \langle ab|ji\rangle
\end{aligned}$$

Appendix: physical constants

Speed of light in vacuum	$c = 2.9979 \times 10^{8}\,\mathrm{ms}^{-1}$
Permittivity of free space	$\epsilon_0 = 8.854 \times 10^{-12}\,\mathrm{Fm}^{-1}$
Permeability of free space	$\mu_0 = 4\pi \times 10^{-7}\,\mathrm{Hm}^{-1}$
Electronic charge	$e = 1.6022 \times 10^{-19}\,\mathrm{C}$
Planck constant	$h = 6.626 \times 10^{-34}\,\mathrm{Js}$
	$\hbar = h/2\pi = 1.055 \times 10^{-34}\,\mathrm{Js}$
Boltzmann constant	$k_\mathrm{B} = 1.3807 \times 10^{-23}\,\mathrm{JK}^{-1}$
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	$\mu_\mathrm{B} = 9.274 \times 10^{-24}\,\mathrm{A\,m}^{2}$ (or $\mathrm{J\,T}^{-1}$)