Queen Mary
University of London

M.Sci./M.Sc. Examination

Main Examination Period 2017

SPA7008U-P **Electronic Structure Methods** Duration: 2 hours 30 minutes

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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.

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Examiners: Dr A. J. Misquitta & Dr A. Sapelkin

Question 1

In this question you will explore various aspects of Hartree–Fock theory.

(a)
- Explain why the N-electron wavefunction cannot be represented as a Hartree product (HP):

$$\Psi^{\mathrm{HP}}(x_1, x_2, \cdots, x_N) = \chi_i(x_1)\chi_j(x_2)\cdots\chi_N(x_N),$$

where $x_i = (\mathbf{r}_i, \sigma_i)$ represents both the spatial and spin coordinates of the i^{th} electron, and the $\{\chi_j\}$ are the orthonormal one-electron orbitals.

- Hence explain why the single deteminant form of the wavefunction is suitable for the N-electron wavefunction. Write down the fully normalized form of such a wavefunction and state the mathematical property of the determinant that makes it particularly suitable for this purpose.

[5 marks]

(b)
- Use the Slater–Condon rules presented at the end of this paper to write down an expression for the energy of the N-electron Hamiltonian H with the wavefunction represented as a single determinant. Define each of the terms that appear in this expression.
- What is the physical significance of the exchange term and why does this term appear with a negative sign?

[5 marks]

(c) The Hartree–Fock approximation to the ground state is obtained by optimizing the single-determinant energy with respect to the spin-orbitals. This leads to the following equations for the spin-orbitals

$$\hat{f}|\chi_m\rangle = \epsilon_m|\chi_m\rangle.$$

where the Fock operator $\hat{f}$ is a one-electron effective operator that is given by

$$f(x_1) = h(x_1) + v^{\mathrm{HF}}(x_1),$$

where h is the usual one-electron Hamiltonian and v^{HF} is the Hartree–Fock effective potential that is defined as follows:

$$v^{\mathrm{HF}}(x_1) = \sum_i [\mathcal{J}_i(x_1) - \mathcal{K}_i(x_1)],$$

where the Coulomb and exchange operators are defined as

$$\mathcal{J}_i(x_1)\chi_m(x_1) = \left[\int dx_2 \frac{\chi_i^*(x_2)\ \chi_i(x_2)}{r_{12}}\right]\chi_m(x_1)$$

$$\mathcal{K}_i(x_1)\chi_m(x_1) = \left[\int dx_2 \frac{\chi_i^*(x_2)\ \chi_m(x_2)}{r_{12}}\right]\chi_i(x_1)$$

Now answer the following questions based on this information.

- Explain without proof how the Fock equations may be solved using a basis.
- Why is Hartree–Fock theory referred to as a *self-consistent field* theory?
- Show using the Slater–Condon rules or otherwise that the orbital energy ϵ_m is given by

$$\epsilon_m = \langle m|h|m\rangle + \sum_j \langle mj||mj\rangle$$

  Write down expressions for the energies of an occupied and a virtual orbital.
- Using the following expression for the Hartree–Fock ground-state energy of a system of N electrons,

$$E_0(N) = \sum_i \langle i|h|i\rangle + \frac{1}{2}\sum_{ij} \langle ij||ij\rangle,$$

  prove that the ionization potential to produce an $(N-1)$-electron state with all orbitals frozen and the electron removed from orbital m is $-\epsilon_m$. This is part of Koopman's theorem.

[15 marks]

Question 2

The Kohn–Sham energy functional is defined as

$$E[\rho] = T_S[\rho] + J[\rho] + E_{xc}[\rho] + \int v_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r},$$

where ρ is the electronic density, v_{ext} is the *external* potential, which will normally be the electron–nuclear potential, the kinetic energy functional is defined as

$$T_S[\rho] = \sum_i^N -\frac{1}{2}\langle\chi_i|\nabla^2|\chi_i\rangle,$$

where χ_i are the N occupied spin-orbitals of the system, the Coulomb energy functional is defined as

$$J[\rho] = \frac{1}{2}\iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2,$$

and $E_{xc}[\rho]$ is the exchange-correlation functional.

(a) Minimize $E[\rho]$ subject to the orthonormality constraints

$$\langle\chi_i|\chi_j\rangle = \delta_{ij},$$

to show that you obtain the non-canonical form of the Kohn–Sham equations:

$$\hat{k}|\chi_i\rangle = \sum_j \epsilon_{ji}|\chi_j\rangle$$

where the Kohn–Sham operator is defined as

$$\hat{k} = -\frac{1}{2}\nabla^2 + v_S(\mathbf{r}).$$

Define the effective potential $v_S(\mathbf{r})$.

[10 marks]

(b) Show that because the Kohn–Sham operator, $\hat{k}$, is dependent on the electronic density, it remains invariant if the occupied orbitals are mixed amongst themselves using a unitary transformation:

$$\chi'_i = \sum_j \chi_j U_{ji}$$

where $\mathbf{U}^\dagger = \mathbf{U}^{-1}$. Hence show how the above non-canonical Kohn–Sham equations can be cast into the canonical form using a particular kind of unitary transformation.

[7 marks]

(c) Describe with a sufficient amount of detail any two classes of exchange-correlation functional. Provide examples of functionals in these classes.

[4 marks]

(d) Describe two shortcomings of standard density functionals and techniques for (partially) overcoming these problems.

[4 marks]

Question 3

Consider the perturbed Hamiltonian

$$\mathcal{H} = \mathcal{H}^{(0)} + \lambda \mathcal{H}^{(1)},$$

where $\mathcal{H}^{(0)}$ is the unperturbed Hamiltonian, $\mathcal{H}^{(1)}$ is the perturbation, and λ is an order parameter that will be set to 1 for the physical system. Assume that the eigenfunctions of $\mathcal{H}^{(0)}$ are given by

$$\mathcal{H}^{(0)}\Psi_n^{(0)} = E_n^{(0)}\Psi_n^{(0)}.$$

Let ϕ be a trial first-order wavefunction for the ground state of this Hamiltonian so that the trial wavefunction to first order is

$$\tilde{\Psi}_0 = \Psi_0^{(0)} + \lambda\phi.$$

Additionally assume that $\langle \Psi_0^{(0)}|\phi\rangle = 0$.

(a) Show that

$$\begin{aligned}\langle E\rangle &= \frac{\langle \tilde{\Psi}_0|\mathcal{H}|\tilde{\Psi}_0\rangle}{\langle \tilde{\Psi}_0|\tilde{\Psi}_0\rangle} \\ &= E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 X^{(2)} + \mathcal{O}(\lambda^3),\end{aligned}$$

where

$$X^{(2)} = \langle\phi|\mathcal{H}^{(0)} - E_0^{(0)}|\phi\rangle + \langle\phi|\mathcal{H}^{(1)}|\Psi_0^{(0)}\rangle + \langle\Psi_0^{(0)}|\mathcal{H}^{(1)}|\phi\rangle,$$

and $E_0^{(1)}$ is the first-order energy correction in Rayleigh–Schrödinger perturbation theory. **[7 marks]**

(b) Hence show that $X^{(2)} \geq E_0^{(2)}$, where $E_0^{(2)}$ is the second-order Rayleigh–Schrödinger energy correction that satisfies the relation

$$(\mathcal{H}^{(0)} - E_0^{(0)})\Psi_0^{(1)} = -(\mathcal{H}^{(1)} - E_0^{(1)})\Psi_0^{(0)}.$$

[8 marks]

(c) Choose ϕ to have the particular form

$$\phi = \sum_{i>0} c_i \Psi_i^{(0)},$$

where the c_i are treated as variational coefficients. Find the variationally optimized values of these coefficients, and hence show that at its optimal value, $X^{(2)} = E_0^{(2)}$.

[10 marks]

Question 4

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, for an atom, the effective potential is defined as

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

(a) Use an asymptotic analysis to show that for a neutral atom,

$$v_{\mathrm{S}}(\mathbf{r}) \rightarrow -\frac{1}{r}$$

as $r \rightarrow \infty$. Hence show that

$$v_{\mathrm{xc}}(\mathbf{r}) \rightarrow -\frac{1}{r},$$

as $r \rightarrow \infty$.

[8 marks]

(b) Prove the equivalent of Koopman's theorem for density functional theory. This states that

$$E_I = -\epsilon_{\mathrm{HOMO}},$$

where E_I is the (first) vertical ionization energy and ϵ_{HOMO} is the energy of the *highest occupied molecular orbital*. You may use the fact that the exact density has the asymptotic form

$$\rho(\mathbf{r}) \rightarrow \exp\left(-2\sqrt{2E_I}r\right).$$

HINT: Use an asymptotic analysis of the Kohn–Sham equation to show that the Kohn–Sham orbitals must satisfy the asymptotic form: $\chi_i(\mathbf{r}) \rightarrow \exp\left(-\sqrt{-2\epsilon_i}r\right)$, and then use this result to find out the asymptotic form of the Kohn–Sham electron density.

[12 marks]

(c) Standard local and semi-local density functionals are known to have difficulty in describing anions (negatively charged ions). Use an asymptotic analysis of $v_{\mathrm{S}}(\mathbf{r})$ and your knowledge of local functionals to explain why this might be the case. How might this problem be alleviated?

[5 marks]

Question 5

(a) Explain what is meant by *size-extensivity*. Why do approximate methods to solve the Schrödinger equation need to be size-extensive?

[5 marks]

(b) Explain why truncated configuration-interaction methods like CID (CI with double excitations only) are not size-extensive.

[5 marks]

(c) For the next two parts of this question you will construct the CID wavefunctions for a single helium atom, and then a collection of N non-interacting helium atoms.

Consider a single helium atom with a Hartree–Fock ground state wavefunction Ψ_0 and doubly excited wavefunction χ. Assume the following:

$$\begin{aligned}\langle\Psi_0|\Psi_0\rangle &= 1\\ \langle\chi|\chi\rangle &= 1\\ \langle\Psi_0|\chi\rangle &= 0\\ \langle\Psi_0|\hat{h}|\Psi_0\rangle &= \epsilon_0\\ \langle\Psi_0|\hat{h}|\chi\rangle &= \beta\\ \langle\chi|\hat{h}|\chi\rangle &= \alpha\end{aligned}$$

Here $\hat{h}$ is the Hamiltonian for the single atom.

(i) The CID wavefunction for this atom may be written as

$$\Psi = \Psi_0 + c\,\chi,$$

where c is a constant. Set up and solve the CID equations for this system and find the CID energy. Hence define the correlation energy, ϵ_{corr}, for this system.

[5 marks]

(ii) Now consider a system of N non-interacting helium atoms with Hamiltonian $\hat{H} = \sum_{i=1}^{N} \hat{h}_i$. The reference ground state for this system is given by

$$\Phi_0 = \mathcal{A}\{\Psi_0(1)\Psi_0(2)\cdots\Psi_0(N)\},$$

where $\Psi_0(i)$ is the reference state for atom i and $\mathcal{A}$ is the antisymmetrization operator.

Doubly excited states have the form

$$\Phi_i = \mathcal{A}\{\Psi_0(1)\cdots\Psi_0(i-1)\chi(i)\Psi_0(i+1)\cdots\Psi_0(N)\},$$

where Ψ_i is a state with the i^{th} atom excited into doubly excited state $\chi(i)$.

α) Write down the CID wavefunction in terms of these states. Is there any symmetry you can use to simplify the problem?

[2 marks]

β) Setup and solve the CID equations for the CID energy of this system. Hence obtain the CID correlation energy, $E_{\text{corr}}^{\text{CID}}$, for this system.
HINT: Use the Slater–Condon rules to evaluate the matrix elements of the Hamiltonian.

[6 marks]

γ) What should be the exact correlation energy, E_{corr}, of this system? Show that $E_{\text{corr}}^{\text{CID}}/E_{\text{corr}} \to 0$ as $N \to \infty$.

[2 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 $\mathrm{J\,T^{-1}}$)