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

Thursday 28^{th} May 2015 10:00–12:30

SPA7008U-P/PHY7016P **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.

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

Question 1

(a) The 1-electron Hamiltonian in a central potential is given by

$$\begin{aligned}\mathcal{H} &= -\frac{1}{2}\nabla^2 + V(\mathbf{r}) \\ &= -\frac{1}{2}(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{\hat{l}^2}{r^2}) - \frac{Z}{r}.\end{aligned}$$

Use this Hamiltonian to show that the exact, spherically symmetric wavefunction Ψ satisfies the electron–nuclear cusp condition

$$\left.\frac{\partial \Psi}{\partial r}\right|_{r=0} = -Z\Psi(r=0),$$

where r is the electron–nuclear separation and Z is the nuclear charge.

Without proof, state how this condition is modified for the general (possibly non-spherically symmetric) wavefunction.

[8 marks]

(b) Show that for the general 1-electron wavefunction Ψ_1 with energy eigenvalue $E_1 < 0$ (i.e., a bound state), as $r \rightarrow \infty$

$$\Psi_1 \rightarrow e^{-\sqrt{-2E_1}r}.$$

Extend this proof to the N-electron wavefunction Ψ_N to show that

$$\Psi_N \rightarrow \Psi_{N-1} e^{-\sqrt{2E_I}r},$$

where Ψ_{N-1} is an $N-1$ electron state and E_I is the vertical ionisation energy defined as $E_I = E_{N-1} - E_N$.

[12 marks]

(c) Gaussian basis sets commonly used as an expansion bases for the wavefunction consist of functions of the form:

$$G_n(\mathbf{r}; i, j, k, \alpha_n, \mathbf{A}_n) = N x^i y^j z^k e^{-\alpha_n(\mathbf{r}-\mathbf{A}_n)^2},$$

where i, j, and k are suitable integers, α_n is a constant, N is the normalization constant, and $\mathbf{A}_n$ is the centre (usually the nuclear position) on which the function is located. Explain how, though these basis functions do not satisfy either of the above conditions, yet they can still be used as expansion basis functions to model the wavefunction. You may simplify your discussion by considering the special case of $i = j = k = 0$ and $\mathbf{A}_n = (0, 0, 0)$.

[5 marks]

Question 2

(a) Show that the exact exchange-correlation potential behaves as $v_{\rm XC} \rightarrow -1/r$ as $r \rightarrow \infty$. State two properties that depend strongly on this property of $v_{\rm XC}$.

[7 marks]

(b) The exchange-correlation potential for the LB94 potential 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 $r \rightarrow \infty$, $n \rightarrow e^{-\alpha r}$, where α is a constant. Show that in this limit $v_{\rm XC}^{\rm LB94} \rightarrow -1/r$.

You may find one or both of these results useful:

$$\sinh^{-1}(x) \rightarrow x \quad \text{as} \quad x \rightarrow 0$$
$$\sinh^{-1}(x) \rightarrow -\ln(x^{-1}) \quad \text{as} \quad x \rightarrow \infty$$

[10 marks]

(c) Explain why excitation energies (particularly Rydberg excitations) are well described by LB94 but not by functionals like PBE. Explain why the converse is true for properties that depend on the core electronic density (such as bond-lengths and dipole moments): these are significantly better described using PBE than the LB94 functional.

[8 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 and sketch the normalized symmetry-adapted atomic orbitals for H_2.

(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?

[8 marks]

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

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

where τ 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 τ 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.

[17 marks]

You will find the following result useful:
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.

Question 4

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

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

and hence $\rho_\alpha(\mathbf{r}) = \alpha^3\rho(\alpha\mathbf{r})$.

(a) It can be shown that under coordinate scaling, the electron-electron interaction energy $V_{\text{ee}}[\rho_\alpha] = \alpha V_{\text{ee}}[\rho]$. Since the exchange energy functional $E_x[\rho]$ is part of $V_{\text{ee}}[\rho]$ 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 ρ, 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) Derive the Slater exchange *potential* $v_x(\mathbf{r})$.

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

[15 marks]

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

(ii) The correlation potential v_{c} is known to be short-ranged, hence the above asymptotic form results from the exchange potential: i.e., $v_{\text{x}} \to -1/r$. 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.

[10 marks]

Question 5

The many-body Hamiltonian $\mathcal{H}$ may be partitioned as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{V},$$

where $\mathcal{H}_0 = \sum_i f(i)$ is the Hartree–Fock (HF) Hamiltonian and the operator $\mathcal{V}$ is defined as

$$\begin{aligned}\mathcal{V} &= \mathcal{H} - \mathcal{H}_0 \\ &= \sum_{i>j} r_{ij}^{-1} - \sum_i v^{\mathrm{HF}}(i).\end{aligned}$$

Here i and j label electronic variables and v^{HF} is the Hartree–Fock effective potential that is defined by its action on spin-orbital $|i\rangle$ as follows:

$$v^{\mathrm{HF}}|i\rangle = \sum_j \langle j|r_{12}^{-1}|j\rangle|i\rangle - \sum_j \langle j|r_{12}^{-1}|i\rangle|j\rangle.$$

The many-body perturbation theory (MBPT) expansion is developed by treating $\mathcal{V}$ as a perturbation and using Raleigh–Schrödinger perturbation theory to evaluate the energy corrections, the first three of which are:

$$\begin{aligned}E_0^{(0)} &= \langle\Psi_0^{(0)}|\mathcal{H}_0|\Psi_0^{(0)}\rangle \\ E_0^{(1)} &= \langle\Psi_0^{(0)}|\mathcal{V}|\Psi_0^{(0)}\rangle \\ E_0^{(2)} &= \langle\Psi_0^{(0)}|\mathcal{V}|\Psi_0^{(1)}\rangle \\ &= \sum_n{}' \frac{|\langle 0|\mathcal{V}|n\rangle|^2}{E_0^{(0)} - E_n^{(0)}}\end{aligned}$$

where $|\Psi_0^{(0)}\rangle = |0\rangle$ is the HF ground state and $|n\rangle$ are the excited states.

Solve the two parts to this question using the following results:
For a Hamiltonian $\mathcal{H} = \sum_i h(i) + \sum_{i>j} r_{ij}^{-1}$

$$\begin{aligned}\langle\Psi|\mathcal{H}|\Psi\rangle &= \sum_i \langle i|h|i\rangle + \sum_{i>j}\langle ij||ij\rangle \\ \langle\Psi_{ij}^{ab}|\mathcal{H}|\Psi\rangle &= \langle\Psi_{ij}^{ab}|\sum_{kl} r_{kl}^{-1}|\Psi\rangle = \langle ij||ab\rangle\end{aligned}$$

(a) Show that the terms $E_0^{(0)}$ and $E_0^{(1)}$ are included in the HF ground state energy. That is

$$E_0^{(0)} + E_0^{(1)} = E_0^{\mathrm{HF}} = \sum_i \epsilon_i - \frac{1}{2}\sum_{ij}\langle ij||ij\rangle.$$

[10 marks]

(b) Hence the first term in the MBPT expansion that contributes beyond HF is $E_0^{(2)}$. Show that the only excited states $|n\rangle$ that contribute to $E_0^{(2)}$ are double excitations from the

HF ground state $|0\rangle$. Hence show that the second-order MBPT energy correction can be written as

$$E_0^{(2)} = \sum_{i>j,a>b} \frac{|\langle ij||ab\rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

where i and j label occupied states and a and b label virtual states, ϵ_n is the orbital energy of the one-electron state χ_n and $\langle ij||ab\rangle = \langle ij|ij\rangle - \langle ij|ji\rangle$.

[15 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	$\mu_\mathrm{B} = 9.274 \times 10^{-24}\ \mathrm{A\ m^2}\quad (\mathrm{or\ J\,T^{-1}})$