FALL 2021 EXAMINATION II

Duration: 150 mins

There are 8 questions (total 30 marks). Answer all questions.

A permitted calculator may be used.

1. (3 marks) Write the Hamiltonian for H_2 and indicate the terms that comprise the electronic Hamiltonian.

$\hat{H} = -\frac{1}{2M_1}\nabla^2_{\mathbf{R}_1} - \frac{1}{2M_2}\nabla^2_{\mathbf{R}_2} - \frac{1}{2}\nabla^2_{\mathbf{r}_1} - \frac{1}{2}\nabla^2_{\mathbf{r}_2} - \frac{1}{|\mathbf{R}_1-\mathbf{R}_2|} - \frac{1}{|\mathbf{r}_1-\mathbf{R}_1|} - \frac{1}{|\mathbf{r}_2-\mathbf{R}_1|} - \frac{1}{|\mathbf{r}_1-\mathbf{R}_2|} - \frac{1}{|\mathbf{r}_2-\mathbf{R}_2|} + \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}$

$\hat{H}_{elec} = -\frac{1}{2}\nabla^2_{\mathbf{r}_1} - \frac{1}{2}\nabla^2_{\mathbf{r}_2} - \frac{1}{|\mathbf{r}_1-\mathbf{R}_1|} - \frac{1}{|\mathbf{r}_2-\mathbf{R}_1|} - \frac{1}{|\mathbf{r}_1-\mathbf{R}_2|} - \frac{1}{|\mathbf{r}_2-\mathbf{R}_2|} + \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}$

2. (3 marks) Determine the number of cartesian contracted and primitive Gaussian functions in a molecular electronic structure calculation on ethanal CH_3CHO using (i) 6-31G (ii) 6-31G* and (iii) 6-31+G* basis sets.

   i) 35 contracted Gaussian functions, 82 primitive Gaussian functions

   ii) Cartesian d-orbitals:
       53 contracted Gaussian functions, 100 primitive Gaussian functions

   iii) Cartesian d-orbitals:
        65 contracted Gaussian functions, 112 primitive Gaussian functions

3. (4 marks) Write the following integrals in bra-ket notation:

   i) $\int f^*(x)g(x)dx$

   $$\langle f(x)|g(x)\rangle \tag{1}$$

   ii) $\int f(\tau)g(\tau)d\tau$

   $$\langle f^*(\tau)|g(\tau)\rangle \tag{2}$$

   iii) $(\hat{H} + x^2)\psi(x) = E\psi(x)$

   $$(\hat{H} + x^2)|\psi(x)\rangle = E|\psi(x)\rangle \tag{3}$$

iv) $\psi(x) \int \psi^*(x') f(x') dx' + 3g(x)$

$$|\psi(x)\rangle \langle \psi(x')|f(x')\rangle + 3|g(x)\rangle \tag{4}$$

4. (4 marks) Compute the Hückel molecular orbital energies of propene.

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = 0$$

$$\begin{vmatrix} -x & 1 & 0 \\ 1 & -x & 1 \\ 0 & 1 & -x \end{vmatrix} = 0$$

$-x(x^2 - 1) + x = x(-x^2 + 2) = 0$

$x = 0, \pm\sqrt{2} \quad E_0 = \alpha + \sqrt{2}\beta, \; E_1 = \alpha, \; E_2 = \alpha - \sqrt{2}\beta$

5. (4 marks) Confirm that the matrices $\mathbf{s}_w = \frac{\hbar}{2}\boldsymbol{\sigma}_w$, where $w = \{x, y, z\}$ and $\boldsymbol{\sigma}_w$ are the Pauli spin matrices, form a representation of angular momentum. Show that these matrices are a representation of $s = \frac{1}{2}$. The Pauli spin matrices are:

$$\boldsymbol{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \boldsymbol{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \boldsymbol{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

To demonstrate the matrices are a representation of angular momentum, we must show they obey the commutation relations.

$$[\mathbf{s}_x, \mathbf{s}_y] = \frac{\hbar}{2}\boldsymbol{\sigma}_x \frac{\hbar}{2}\boldsymbol{\sigma}_y - \frac{\hbar}{2}\boldsymbol{\sigma}_y \frac{\hbar}{2}\boldsymbol{\sigma}_x = \frac{\hbar^2}{4}\left\{ \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} - \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \right\}$$

$$= \frac{\hbar^2}{4}\left\{ \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} - \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix} \right\} = \frac{\hbar^2}{4}\begin{pmatrix} 2i & 0 \\ 0 & -2i \end{pmatrix} = i\hbar\frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = i\hbar\mathbf{s}_z$$

Construct the matrix representation of $\mathbf{s}^2$ and then extract eigenvalues which should be $s(s+1)\hbar^2$ then solve for s.

$$\mathbf{s}^2 = \mathbf{s}_x^2 + \mathbf{s}_y^2 + \mathbf{s}_z^2 = \frac{\hbar^2}{4}\left\{ \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right\}$$

$$= \frac{\hbar^2}{4}\left\{ \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \right\} = \frac{3\hbar^2}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

As $s(s+1) = \frac{3}{4}$, so $s = 1/2$

6. (4 marks) Write the electronic energy of a restricted-open shell Slater determinant representing the i) doublet and ii) quartet wavefunction of BeH.

$$^2E_{\text{ROHF}} = 2h_{11} + 2h_{22} + h_{33} + J_{11} + J_{22} + 4J_{12} + 2J_{13} + 2J_{23} - 2K_{12} - K_{13} - K_{23} \tag{5}$$

$$^4E_{\text{ROHF}} = 2h_{11}+h_{22}+h_{33}+h_{44}+J_{11}+2J_{12}+2J_{13}+2J_{14}+J_{23}+J_{24}+J_{34}-K_{12}-K_{13}-K_{14}-K_{23}-K_{24}-K_{34} \tag{6}$$

7. (4 marks) Consider the ground state of the hydrogen molecule with a wavefunction represented by a restricted Slater determinant, such that two electrons occupy the same spatial orbital $\psi_1(\mathbf{r})$.

    i) Write out explicitly the terms contained in the Fock operator for one of the electrons.

$$\hat{F} = \hat{h} + \hat{J}_2 \tag{7}$$

    ii) Compute the orbital energy of the electron described by the Fock operator in part i).

$$\langle\psi_1|\hat{F}|\psi_1\rangle = \langle\psi_1|\hat{h}|\psi_1\rangle + \langle\psi_1|\hat{J}_2|\psi_1\rangle = \langle\psi_1|\hat{h}|\psi_1\rangle + \langle\psi_1\psi_2|\psi_2\psi_1\rangle = h_{11} + J_{12} = \varepsilon_1 \tag{8}$$

    iii) Write down the ionization energy of the electron in part ii) according to Koopmans' theorem.

$$\text{IE} = -\varepsilon_1 \tag{9}$$

    iv) Write the approximations involved in computing ionization energies using Koopmans' theorem.

        • Orbital relaxation in response to ionization

        • Electron correlation (going beyond mean-field approximation)

8. (4 marks) Given the Slater determinant wavefunction $|\Psi\rangle = N|\psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)\rangle$, determine the normalization constant N.

$$N^2 \langle \psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)|\psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)\rangle = 1$$

$$N^2 \langle \{\psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2) - \psi_1(\mathbf{x}_2)\psi_2(\mathbf{x}_1)\}|\{\psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2) - \psi_1(\mathbf{x}_2)\psi_2(\mathbf{x}_1)\}\rangle = 1$$

$$N^2 \{\langle \psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)|\psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)\rangle + \langle \psi_1(\mathbf{x}_2)\psi_2(\mathbf{x}_1)|\psi_1(\mathbf{x}_2)\psi_2(\mathbf{x}_1)\rangle$$
$$- \langle \psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)|\psi_1(\mathbf{x}_2)\psi_2(\mathbf{x}_1)\rangle - \langle \psi_1(\mathbf{x}_2)\psi_2(\mathbf{x}_1)|\psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)\rangle\} = 1$$

$$N^2 \{\langle \psi_1(\mathbf{x}_1)|\psi_1(\mathbf{x}_1)\rangle\langle \psi_2(\mathbf{x}_2)|\psi_2(\mathbf{x}_2)\rangle + \langle \psi_1(\mathbf{x}_2)|\psi_1(\mathbf{x}_2)\rangle\langle \psi_2(\mathbf{x}_1)|\psi_2(\mathbf{x}_1)\rangle$$
$$- \langle \psi_1(\mathbf{x}_1)|\psi_2(\mathbf{x}_1)\rangle\langle \psi_2(\mathbf{x}_2)|\psi_1(\mathbf{x}_2)\rangle - \langle \psi_2(\mathbf{x}_1)|\psi_1(\mathbf{x}_1)\rangle\langle \psi_1(\mathbf{x}_2)|\psi_2(\mathbf{x}_2)\rangle\} = 1$$

$$N^2 \{1 \times\ 1 + 1 \times 1 - 0 \times 0 - 0 \times 0\} = 1$$

$$2N^2 = 1$$

$$N = \frac{1}{\sqrt{2}}$$

END OF PAPER