EST Problem 1: Selected Solutions

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Abstract

Here I give a step-by-step solution to Q8 and Q10 of Prof Tew's EST worksheet 1.

Problem 8

Let's begin with a simple two-electron case to understand how terms drop out, then generalize. For two electrons, the Slater determinant is:

$$|\Psi\rangle = \sqrt{2!}\hat{A}\,|\phi_1\phi_2\rangle = \frac{1}{\sqrt{2}}(|\phi_1\phi_2\rangle - |\phi_2\phi_1\rangle) \tag{1}$$

Let's evaluate $\rho(x)$ for this two-electron case:

$$\begin{aligned}\rho(x) &= \langle\Psi|\,[\delta(x-x_1)+\delta(x-x_2)]\,|\Psi\rangle \qquad (2)\\ &= \frac{1}{2}\big(\,\langle\phi_1\phi_2| - \langle\phi_2\phi_1|\,\big)[\delta(x-x_1)+\delta(x-x_2)]\big(\,|\phi_1\phi_2\rangle - |\phi_2\phi_1\rangle\,\big) \qquad (3)\end{aligned}$$

Let's focus on $\delta(x-x_1)$ terms first:

$$\begin{aligned}&\frac{1}{2}\big[\,\langle\phi_1\phi_2|\,\delta(x-x_1)\,|\phi_1\phi_2\rangle\\ &-\langle\phi_1\phi_2|\,\delta(x-x_1)\,|\phi_2\phi_1\rangle\\ &-\langle\phi_2\phi_1|\,\delta(x-x_1)\,|\phi_1\phi_2\rangle\\ &+\langle\phi_2\phi_1|\,\delta(x-x_1)\,|\phi_2\phi_1\rangle\,\big]\end{aligned} \tag{4}$$

We can now evaluate each term:

- Term 1: $\langle\phi_1\phi_2|\,\delta(x-x_1)\,|\phi_1\phi_2\rangle$

$$= |\phi_1(x)|^2\,\langle\phi_2|\phi_2\rangle = |\phi_1(x)|^2 \tag{5}$$

- Term 2: $\langle \phi_1\phi_2 |\, \delta(x - x_1)\, | \phi_2\phi_1 \rangle$

$$= \phi_1^*(x)\phi_2(x)\, \langle \phi_2 | \phi_1 \rangle = 0 \tag{6}$$

  due to orbital orthogonality

- Term 3: $\langle \phi_2\phi_1 |\, \delta(x - x_1)\, | \phi_1\phi_2 \rangle$

$$= \phi_2^*(x)\phi_1(x)\, \langle \phi_1 | \phi_2 \rangle = 0 \tag{7}$$

  also due to orbital orthogonality

- Term 4: $\langle \phi_2\phi_1 |\, \delta(x - x_1)\, | \phi_2\phi_1 \rangle$

$$= |\phi_2(x)|^2\, \langle \phi_1 | \phi_1 \rangle = |\phi_2(x)|^2 \tag{8}$$

Following the same process for $\delta(x - x_2)$ terms:

$$\begin{aligned} &\frac{1}{2}\Big[\, \langle \phi_1\phi_2 |\, \delta(x - x_2)\, | \phi_1\phi_2 \rangle \\ &- \langle \phi_1\phi_2 |\, \delta(x - x_2)\, | \phi_2\phi_1 \rangle \\ &- \langle \phi_2\phi_1 |\, \delta(x - x_2)\, | \phi_1\phi_2 \rangle \\ &+ \langle \phi_2\phi_1 |\, \delta(x - x_2)\, | \phi_2\phi_1 \rangle \,\Big] \end{aligned} \tag{9}$$

Again, cross terms drop out due to orthogonality, leaving us with:

$$\frac{1}{2}(|\phi_2(x)|^2 + |\phi_1(x)|^2) \tag{10}$$

Adding all surviving terms:

$$\begin{aligned} \rho(x) &= \frac{1}{2}(|\phi_1(x)|^2 + |\phi_2(x)|^2) + \frac{1}{2}(|\phi_2(x)|^2 + |\phi_1(x)|^2) \qquad (11) \\ &= |\phi_1(x)|^2 + |\phi_2(x)|^2 \qquad (12) \end{aligned}$$

Generalization to N Electrons

For the N-electron case, the same pattern holds but with more terms. The key points remain:

1. Direct terms ($\langle \phi_i\phi_j |\, \delta(x - x_k)\, | \phi_i\phi_j \rangle$) survive and contribute $|\phi_i(x)|^2$
2. Cross terms ($\langle \phi_i\phi_j |\, \delta(x - x_k)\, | \phi_j\phi_i \rangle$) vanish due to orthogonality
3. The normalization factor $\frac{1}{N!}$ from $\hat{A}$ exactly balances the number of equivalent permutations

Therefore, in general:

$$\rho(x) = \sum_i |\phi_i(x)|^2 \tag{13}$$

Double Occupation Case

For doubly occupied spatial orbitals $\varphi_j(r)$:

$$\rho_\alpha(r) = \sum_j |\varphi_j(r)|^2 = \rho_\beta(r) \tag{14}$$

The equality holds because each spatial orbital contributes identically to both α and β spin densities.

Problem 10 Part (a): Molecular Orbital Coefficients

Given Information

- MOs are linear combinations: $\sigma_g = \chi_A C_{Ag} + \chi_B C_{Bg}$ and $\sigma_u = \chi_A C_{Au} + \chi_B C_{Bu}$
- 1s functions are normalized: $\langle \chi_A | \chi_A \rangle = \langle \chi_B | \chi_B \rangle = 1$
- Overlap integral: $\langle \chi_A | \chi_B \rangle = S$

Finding the MO Coefficients

Using symmetry properties:

- σ_g is symmetric: $C_{Ag} = C_{Bg}$
- σ_u is antisymmetric: $C_{Au} = -C_{Bu}$

Let's impose normalization:
For σ_g:

$$\begin{aligned} 1 &= \langle \sigma_g | \sigma_g \rangle \\ &= (C_{Ag}^2 + C_{Bg}^2 + 2C_{Ag}C_{Bg}S) \\ &= 2C_{Ag}^2(1+S) \end{aligned} \tag{15}$$

Therefore:

$$C_{Ag} = C_{Bg} = \frac{1}{\sqrt{2(1+S)}} \tag{16}$$

For σ_u:

$$\begin{aligned} 1 &= \langle \sigma_u | \sigma_u \rangle \\ &= (C_{Au}^2 + C_{Bu}^2 - 2C_{Au}C_{Bu}S) \\ &= 2C_{Au}^2(1-S) \end{aligned} \tag{17}$$

Therefore:

$$C_{Au} = -C_{Bu} = \frac{1}{\sqrt{2(1-S)}} \tag{18}$$

Verifying Orthonormality

The coefficient matrix **C** is:

$$\mathbf{C} = \begin{pmatrix} \frac{1}{\sqrt{2(1+S)}} & \frac{1}{\sqrt{2(1-S)}} \\ \frac{1}{\sqrt{2(1+S)}} & -\frac{1}{\sqrt{2(1-S)}} \end{pmatrix} \tag{19}$$

Let's verify orthonormality:

$$\mathbf{C}^{\mathsf{T}} \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix} \mathbf{C} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{20}$$

Problem 10 Part (b): Kinetic Energy Analysis

The kinetic energy expectation value is:

$$\langle\psi| \hat{T} |\psi\rangle = 2 \langle\sigma_g| (-\frac{1}{2}\nabla^2) |\sigma_g\rangle + 2 \langle\sigma_u| (-\frac{1}{2}\nabla^2) |\sigma_u\rangle \tag{21}$$

Qualitative Analysis of Kinetic Energy

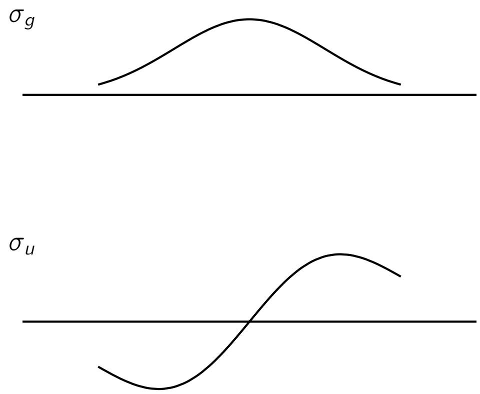

Figure 1: Schematic representation of σ_g and σ_u orbitals

The σ_u orbital has a node and more spatial variation, leading to larger kinetic energy:

$$\langle\sigma_u| (-\frac{1}{2}\nabla^2) |\sigma_u\rangle > \langle\sigma_g| (-\frac{1}{2}\nabla^2) |\sigma_g\rangle \tag{22}$$

Part (c): Coulomb and Exchange Energies

Using the properties of Slater determinant wavefunctions, we derive:

Coulomb Energy

$$J = 2\langle\sigma_g\sigma_g|\, r_{12}^{-1}\,|\sigma_g\sigma_g\rangle + 4\langle\sigma_g\sigma_u|\, r_{12}^{-1}\,|\sigma_g\sigma_u\rangle + 2\langle\sigma_u\sigma_u|\, r_{12}^{-1}\,|\sigma_u\sigma_u\rangle \tag{23}$$

This represents:

- Direct interaction between electrons in σ_g orbitals
- Cross-interaction between σ_g and σ_u electrons
- Direct interaction between electrons in σ_u orbitals

Exchange Energy

$$K = \langle\sigma_g\sigma_g|\, r_{12}^{-1}\,|\sigma_g\sigma_g\rangle + 2\langle\sigma_g\sigma_u|\, r_{12}^{-1}\,|\sigma_u\sigma_g\rangle + \langle\sigma_u\sigma_u|\, r_{12}^{-1}\,|\sigma_u\sigma_u\rangle \tag{24}$$

The exchange terms arise from:

- Exchange between same-spin electrons in σ_g orbitals
- Exchange between same-spin electrons in σ_g and σ_u orbitals
- Exchange between same-spin electrons in σ_u orbitals

Physical Interpretation

1. The molecular orbitals maintain proper symmetry (σ_g symmetric, σ_u antisymmetric)
2. The normalization factors depend on the atomic orbital overlap S, showing how bonding affects orbital structure
3. The higher kinetic energy of σ_u reflects the antibonding nature of this orbital
4. The Coulomb and exchange energies show both intra-orbital and inter-orbital electron interactions
5. The factor of 2 in various terms reflects the double occupation of orbitals