

## Exercises: Basic Quantum Mechanics

1. Consider a particle of mass  $m$  confined to move on a sphere of radius  $a$ .
  - a. Express the Hamiltonian operator in spherical coordinates and determine energy levels and wave functions.
2. Consider a particle of mass  $m$  in a one-dimensional potential such that

$$V(x) = \begin{cases} 0, & -a/2 \leq x \leq a/2 \\ \infty, & x < -a/2, \quad x > a/2 \end{cases}$$

Solve the time-independent Schrödinger equation for this particle to obtain the energy levels and normalized wave functions.

3. Which of the following operators are linear?
  - a)  $\sqrt{\cdot}$
  - b)  $\sin(\cdot)$
  - c)  $x \frac{d}{dx}$
  - d)  $\frac{d}{dx} x$
4. Demonstrate the validity of

$$\begin{aligned} [\hat{A}, \hat{B}\hat{C}] &= [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}] \\ [\hat{A}\hat{B}, \hat{C}] &= [\hat{A}, \hat{C}]\hat{B} + \hat{A}[\hat{B}, \hat{C}] \end{aligned}$$

5. Show that

$$[\hat{A}, [\hat{B}, \hat{C}]] + [\hat{B}, [\hat{C}, \hat{A}]] + [\hat{C}, [\hat{A}, \hat{B}]] = 0$$

where  $\hat{A}$ ,  $\hat{B}$ , and  $\hat{C}$  are arbitrary linear operators.

6. Show that

$$\left(\frac{d}{dx} + x\right) \left(\frac{d}{dx} - x\right) = \frac{d^2}{dx^2} - x^2 - 1$$

7. Show that  $xe^{-x^2}$  is an eigenfunction of the linear operator  $\frac{d^2}{dx^2} - 4x^2$ . What is the eigenvalue?
8. Show that if the linear operators  $\hat{A}$  and  $\hat{B}$  do not commute, the operators  $(\hat{A}\hat{B} + \hat{B}\hat{A})$  and  $i[\hat{A}, \hat{B}]$  are Hermitian.
9. If the real normalized functions  $f(x)$  and  $g(x)$  are not orthogonal, show that their sum  $f(x) + g(x)$  and their difference  $f(x) - g(x)$  are orthogonal.
10. Evaluate the following commutators:
  - a)  $[x, p_x]$
  - b)  $[x, p_x^2]$
  - c)  $[x, \hat{H}]$
  - d)  $[p_x, \hat{H}]$

11. Show that

$$[x^n, p_x] = i\hbar n x^{n-1}$$

where  $n$  is a positive integer greater than zero.

12. Show that

$$[f(x), p_x] = i\hbar \frac{df(x)}{dx}$$

13. A Hermitian operator  $\hat{A}$  has only three normalized eigenfunctions  $\psi_1, \psi_2, \psi_3$ , with corresponding eigenvalues  $a_1 = 1, a_2 = 2, a_3 = 3$ , respectively. For a particular state  $\Phi$  of the system, there is a 50% chance that a measure of  $A$  produces  $a_1$  and equal chances for either  $a_2$  or  $a_3$ .

a) Calculate  $\langle A \rangle$ .

b) Express the normalized wave function  $\Phi$  of the system in terms of the eigenfunctions of  $\hat{A}$ .

14. If  $|\psi\rangle$  is an eigenfunction of  $\hat{H}$  with eigenvalue  $E$ , show that for any operator  $\hat{A}$  the expectation value of  $[\hat{H}, \hat{A}]$  vanishes, i.e.,

$$\langle \psi | [\hat{H}, \hat{A}] | \psi \rangle = 0$$

## Exercises: Basic Mathematical Review

1. If  $A$  is an  $N \times M$  matrix and  $B$  is a  $M \times K$  matrix show that  $(AB)^\dagger = B^\dagger A^\dagger$ .
2. Show that
  - a)  $\text{tr}AB = \text{tr}BA$
  - b)  $(AB)^{-1} = B^{-1}A^{-1}$
  - c) If  $U$  is unitary and  $B = U^\dagger AU$ , then  $A = UBU^\dagger$ .
  - d) If the product  $C = AB$  of two Hermitian matrices is also Hermitian, then  $A$  and  $B$  commute.
  - e) If  $A$  is Hermitian then  $A^{-1}$ , if it exists is also Hermitian.
  - f) If  $A = \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix}$ , then  $A^{-1} = \frac{1}{A_{11}A_{22} - A_{12}A_{21}} \begin{pmatrix} A_{22} & -A_{12} \\ -A_{21} & A_{11} \end{pmatrix}$
3. Verify for  $2 \times 2$  matrices the properties
  - a) If each element in a row or in a column is zero the value of the determinant is zero.
  - b) If  $(A)_{ij} = A_{ii}\delta_{ij}$ , then  $|A| = \prod_i A_{ii} = A_{11}A_{22} \dots A_{NN}$
  - c) A single interchange of any two rows (or columns) of a matrix changes the sign of its determinant.
  - d)  $|A| = (|A^\dagger|)^*$
  - e)  $|AB| = |A||B|$
4. Prove that in general
  - a) If any two rows (or columns) of a determinant are equal, the value of the determinant is zero.
  - b)  $|A^{-1}| = (|A|)^{-1}$
  - c) If  $AA^\dagger = 1$ , then  $|A|(|A|)^* = 1$ .
  - d) If  $U^\dagger O U = \Omega$  and  $U^\dagger U = 1$ , then  $|O| = |\Omega|$ .
5. Show that the trace of a matrix is invariant under a unitary transformation, i.e., if  $\Omega = U^\dagger O U$  for  $U^\dagger U = 1$  then show that  $\text{tr}\Omega = \text{tr}O$ .
6. Calculate eigenvalues and eigenvectors (normalized) for the matrices

$$A = \begin{pmatrix} 3 & 1 \\ 1 & 3 \end{pmatrix}; \quad B = \begin{pmatrix} 3 & 1 \\ 1 & 2 \end{pmatrix}$$

7. The Schrödinger equation (in atomic units) for the hydrogen atom is

$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r}\right)|\Phi\rangle = \epsilon|\Phi\rangle .$$

Use the variation method with the trial function (variation of  $\alpha$ )

$$|\tilde{\Phi}\rangle = Ne^{-\alpha r^2}$$

to show that  $-\frac{4}{3\pi} \approx -0.4244$  is an upper bound to the exact ground state energy (which is  $-0.4$ ). You will need the relations

$$\begin{aligned}\nabla^2 f(r) &= r^{-2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) f(r) \\ \int_0^\infty dr r^{2m} e^{-\alpha r^2} &= \frac{(2m)! \pi^{1/2}}{2^{2m+1} m! \alpha^{m+1/2}} \\ \int_0^\infty dr r^{2m+1} e^{-\alpha r^2} &= \frac{m!}{2\alpha^{m+1}}\end{aligned}$$

## Exercises: Molecular Hamiltonian

1. Write down the electronic Hamiltonian for  $H_2^+$ .
2. Give a simple approximate solution based on the solution for the Hydrogen atom. (Call the value of the overlap integral between the two  $1s$  orbitals  $S$ )
3. The exact solution for the hydrogen atom gives energies as  $E_n = -\frac{e^2}{2a} \frac{1}{n^2}$ , with  $a = \frac{\hbar^2}{\mu e^2}$  and  $\mu = \frac{m_e m_p}{m_e + m_p}$ . What would be the solution for the hydrogen atom using the Born-Oppenheimer approximation? How big is the error for the ground and first excited state?
4. Write down the general nuclear Hamiltonian for a diatomic molecule.
5. Assume that  $E_{\text{el}}^0$  is  $\frac{1}{2}k(R - R_0)^2$ , where  $R$  is the atomic distance. Calculate the vibrational energy spectrum.

## Exercises: Two-electron Systems and Spin

1. Write down the electronic Hamiltonian for the  $Li^+$  ion.
2. Calculate the total electronic energy assuming no electron-electron interaction.
3. Use variational theory with the wavefunction

$$\Psi(r_1, r_2) = \frac{\eta^3}{\pi a^3} e^{-\frac{\eta}{a}(r_1+r_2)}$$

to calculate a better estimate for the ground state energy.

4. Calculate the total energy of  $Li^{2+}$  and check the literature for the second ionization potential of  $Li$ . Calculate the total energy of  $Li^+$  and compare with the result from the last exercise. Are the errors larger than for  $He$ ?
5. We define two one-electron spin operators

$$s_+ = s_x + is_y; \quad s_- = s_x - is_y$$

Calculate the action of  $s_+$  and  $s_-$  on the eigenfunctions of  $s_z$ .

6. Express the operator  $s^2$  with the operators  $s_+, s_-, s_z$ .
7. Find the  $2 \times 2$  matrix representations of  $s^2, s_z, s_+$ , and  $s_-$  in the basis of  $|\alpha\rangle, |\beta\rangle$ .
8. Calculate the commutation relations between  $s^2, s_z, s_{\pm}$ .
9. Show that  $[s^2, s_z] = 0$  is true.
10. Consider an operator  $\hat{A}$  that commutes with the Hamiltonian. Suppose  $|\Psi\rangle$  is an eigenfunction of  $\hat{H}$  with eigenvalue  $E$ . Show that  $\hat{A}|\Psi\rangle$  is also an eigenfunction of  $\hat{H}$  with eigenvalue  $E$ .
11. Given two nondegenerate eigenfunctions of a Hermitian operator  $\hat{A}$  that commutes with  $\hat{H}$ .

$$\hat{A}|\Psi_1\rangle = a_1|\Psi_1\rangle; \quad \hat{A}|\Psi_2\rangle = a_2|\Psi_2\rangle; \quad a_1 \neq a_2$$

Show that  $\langle \Psi_1 | \hat{H} | \Psi_2 \rangle = 0$ . Thus the matrix element of the Hamiltonian between single and triplet wavefunctions is zero.

## Exercises: Hartree-Fock Approximation

1. How many electrons can be put in each of the following
  - a shell with principal quantum number  $n$
  - a subshell with quantum numbers  $n$  and  $l$
  - an orbital
  - a spin orbital
2. Consider the restricted Hartree-Fock wavefunction for the Helium atom

$$\Psi = 2^{-1/2} \det|\Phi_a^\alpha(1)\Phi_a^\beta(2)|$$

Show that this Slater determinant is an eigenfunction of  $\hat{S}^2$  and evaluate its eigenvalue.

3. Confirm that the unrestricted Hartree-Fock wavefunction for Helium of the form

$$\Psi = 2^{-1/2} \det|\Phi_a(1)\alpha(1)\Phi_b(2)\beta(2)|$$

where  $\Phi_a \neq \Phi_b$  is not an eigenfunction of  $\hat{S}^2$

4. Show that  $(n!)^{-1/2}$  is the correct normalization factor for a single Slater determinant consisting of  $n$  orthonormal spin orbitals.
5. Show that the Slater determinant

$$\Psi = 6^{-1/2} \det|\Phi_a^\alpha(1)\Phi_a^\beta(2)\Phi_a^\alpha(3)|$$

for the  $He^-$  ion is identically zero.

6. Write down the total energy expression for the triplet state of the Helium atom using a Slater determinant wavefunction

$$\Psi = 2^{-1/2} \det|\Phi_a(1)\alpha(1)\Phi_b(2)\alpha(2)|$$

where  $\Phi_a$  and  $\Phi_b$  are orthonormal. Derive the Hartree-Fock equations for this special case. Remove the spin dependence from the equations by integration.

7. Calculate the general matrix element of the Fock operator

$$F_{ij} = \langle \phi_i | \hat{F} | \phi_j \rangle$$

Show that the Fock operator is a Hermitian operator, by showing that  $F_{ij}$  is an element of a Hermitian matrix.

8. Consider the following Slater determinants and their energies

- $|\Psi_0\rangle$ ,  $E_0$ , Hartree-Fock ground state, closed shell restricted determinant
- $|\Psi_c\rangle$ ,  $E_c$ , one electron removed from orbital c
- $|\Psi_{cd}\rangle$ ,  $E_{cd}$ , two electrons removed from orbitals c and d
- $|\Psi^r\rangle$ ,  $E^r$ , one electron added to orbital r

Calculate the following energy differences

- $\text{IP} = E_c - E_0$
- $\text{EA} = E_0 - E^r$
- $E_{cd} - E_0$

## Exercises: Molecular Orbital Theory

1. The Hartree-Fock equations in matrix form are

$$\mathbf{FC} = \mathbf{SCE}$$

where  $\mathbf{F}$  is the Fock matrix,  $\mathbf{C}$  the matrix of the orbital coefficients,  $\mathbf{S}$  the basis function overlap matrix, and  $\mathbf{E}$  the diagonal matrix of orbital energies.

Show that

$$\mathbf{C}^\dagger \mathbf{S} \mathbf{C} = 1$$

2. We define the density operator

$$\hat{\rho}(r) = \sum_{i=1}^N \delta(r_i - r)$$

Show for a Slater determinant  $|\Psi\rangle$  of spin functions  $|\Phi_i\sigma\rangle$  the total density is given by

$$\rho(r) = \langle \Psi | \hat{\rho}(r) | \Psi \rangle$$

3. A matrix  $\mathbf{A}$  is said to be idempotent if  $\mathbf{A}^2 = \mathbf{A}$ . Use  $\mathbf{C}^\dagger \mathbf{S} \mathbf{C} = 1$  and the definition of the density matrix for closed shell functions

$$P_{\mu\nu} = 2 \sum_{a=1}^{N/2} C_{\mu a} C_{\nu a}^*$$

to show that

$$\mathbf{PSP} = 2\mathbf{P}$$

i.e., that  $\frac{1}{2}\mathbf{P}$  would be idempotent in an orthonormal basis.

4. Use the definition of the overlap matrix

$$S_{\mu\nu} = \int \Phi_\mu^*(r) \Phi_\nu(r) dr$$

to show that all eigenvalues of  $\mathbf{S}$  are positive.

## Exercises: Correlation Energy

1. A complete configuration interaction calculation is performed for a minimal basis set (one function per hydrogen atom) for the  $H_2$  molecule. Molecular orbitals from a Hartree-Fock calculation are used to build up the determinantal wave functions.
  - Characterize all possible determinants.
  - Determine the Hamiltonian matrix elements.
2. Give an estimate of the total number of configurations for a calculation of the  $HF$  molecule in a minimal basis.
3. In a CI calculation of the  $^2S$  ground state of lithium, which of the following Slater determinants can contribute to the ground state wavefunction?
  - (a)  $|\Phi_{1s}^\alpha \Phi_{1s}^\beta \Phi_{2s}^\alpha|$
  - (b)  $|\Phi_{1s}^\alpha \Phi_{1s}^\beta \Phi_{2s}^\beta|$
  - (c)  $|\Phi_{1s}^\alpha \Phi_{1s}^\beta \Phi_{2p}^\alpha|$
  - (d)  $|\Phi_{1s}^\alpha \Phi_{2p}^\alpha \Phi_{2p}^\beta|$
  - (e)  $|\Phi_{1s}^\alpha \Phi_{3d}^\alpha \Phi_{3d}^\beta|$
  - (f)  $|\Phi_{1s}^\alpha \Phi_{2s}^\alpha \Phi_{3s}^\alpha|$

4. Hamiltonian matrix elements between two n-electron Slater determinants can be conveniently expressed in terms of integrals over the orthonormal spin orbitals of which the determinants are comprised. Consider two Slater determinants  $\Psi_1$  and  $\Psi_2$  that differ by only one spin orbital; that is,

$$\Psi_1 = \frac{1}{\sqrt{n!}} |\dots \Phi_m \Phi_i \dots| \quad \Psi_2 = \frac{1}{\sqrt{n!}} |\dots \Phi_p \Phi_i \dots|$$

Calculate the matrix element

$$\langle \Psi_1 | \hat{H} | \Psi_2 \rangle .$$

## Exercises: Coupled Cluster Approaches

1. The expression for the Coupled Cluster energy was derived by multiplying the Schrödinger equation from the left with the Hartree-Fock determinant and subsequent integration. Use this method to derive a similar expression for the CI energy.
2. Which of the following methods are capable of yielding an energy below the exact ground state energy?
  - i) Hartree-Fock
  - ii) full CI
  - iii) CISD
  - iv) CCSD
3. Which of the following methods are size consistent?
  - i) Hartree-Fock
  - ii) full CI
  - iii) CISD
  - iv) CCSD
4. Derive an expression for the normalization of the Coupled Cluster wavefunction.

## Exercises: Density Functional Theory

1. What are the essential claims of the Hohenberg–Kohn theorems?
2. What property has to be enforced on the solution of the non-interacting particle system to derive the Kohn–Sham equations? What other property of the solution of the non-interacting particle system is important in deriving the Kohn–Sham equations?
3. The Wigner correlation functional is defined by

$$E_c[\rho] = - \int \frac{0.88}{r_s + 7.8} \rho(r) dr$$

where  $r_s = \left[ \frac{3}{4\pi\rho(r)} \right]^{1/3}$ . What is the formula for the corresponding potential  $V_c(r)$ .

4. You calculate the energy of a molecule using the Hartree–Fock expression with the optimized Kohn–Sham orbitals. What is the relation of this energy with the optimized Hartree–Fock energy? Can you say something about the Kohn–Sham energy calculated using the Hartree–Fock orbitals?
5. What are the three different types of exchange–correlation functionals and what are the basic differences?