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- Exercise 4: Key Choices, Part I
- Post Hartree-Fock Methods
  - Configuration interaction
    - H_2
    - Configuration state functions
    - Configuration interaction levels
  - Moller-Plesset Many-Body Perturbation Theory
  - Density Functional Theory

Exercise: Key Choices

https://colab.research.google.com/github/daveminh/Chem550-2024F/blob/main/exercises/04-Key_Choices.ipynb

Configuration Interaction

Dissociation of H_2

Expected behavior

- As two hydrogen atoms are separated, what value should the energy approach?
- Let's consider what happens when use look at H_2 dissociation using Hartree-Fock with a minimal basis set

Molecular orbitals of H_2^+

- As a reminder, for H_2^+ we found LCAO

- $\sigma_b = \dfrac{1}{\sqrt{2(1+S)}} \left(1s_A(1) + 1s_b(1)\right)$, the bonding orbital

- $\sigma_a = \dfrac{1}{\sqrt{2(1-S)}} \left(1s_A(1) - 1s_b(1)\right)$, the antibonding orbital

The ground state of H_2, D_1

- For H_2, the ground state has two electrons with opposite spins in σ_b. The Slater determinant is,

$$D_1 = \frac{1}{\sqrt{2!}} \begin{vmatrix} \sigma_b\alpha(1) & \sigma_b\beta(1) \\ \sigma_b\alpha(2) & \sigma_b\beta(2) \end{vmatrix} = \sigma_b(1)\sigma_b(2)\left\{ \frac{1}{\sqrt{2}} \left[\alpha(1)\beta(2) - \alpha(2)\beta(1) \right] \right\}$$

- Considering only the spatial part,

$$D_1 = \frac{1}{2(1+S)} \left[1s_A(1) + 1s_B(1) \right] \left[1s_A(2) + 1s_B(2) \right]$$

Results from optimizing D_1

- A reasonable minimum energy of -1.1282 E_h vs -1.1744 E_h experimental
- A reasonable equilibrium distance of 1.385 a_o vs 1.401 a_o experimental
- Incorrect dissociation limit ($R \rightarrow \infty$) compared to isolated H atoms
  - energy, -0.7119 E_h vs -1 E_h
  - decay rate ζ, 0.84375 vs 1

Explaining the dissociation limit

- Expanding the determinant leads to,

$$D_1 = \frac{1s_A(1)1s_B(2) + 1s_A(2)1s_B(1) + 1s_A(1)1s_A(2) + 1s_B(1)1s_B(2)}{2(1 + S)}$$

- What do the different terms describe? Which are covalent and which are ionic?
- In this model, electrons are always 50% covalent and ionic
- At the dissociation limit, H_2 should separate into two neutral atoms; it should be 100% covalent

Consequences of the approximation

- Incorrect dissociation limit ($R \rightarrow \infty$) compared to isolated H atoms
    - of energy, -0.7119 E_h vs -1 E_h
    - of the decay rate, 0.84375 vs 1
- The calculated potential energy well is too steep
- How does this affect the following properties?
    - Dissociation energies
    - Equilibrium bond lengths
    - Vibrational frequencies

Excited states of H_2

- $D_1 = \dfrac{1}{\sqrt{2!}} \begin{vmatrix} \sigma_b\alpha(1) & \sigma_b\beta(1) \\ \sigma_b\alpha(2) & \sigma_b\beta(2) \end{vmatrix}$ is the ground state, based only on σ_b

- There are actually two molecular orbitals and four possible spinorbitals $\sigma_b\alpha, \sigma_b\beta, \sigma_a\alpha, \sigma_a\beta$

- $D_2 = \dfrac{1}{\sqrt{2}} \begin{vmatrix} \sigma_a\alpha(1) & \sigma_a\beta(1) \\ \sigma_a\alpha(2) & \sigma_a\beta(2) \end{vmatrix} = \sigma_a(1)\sigma_a(2) \left\{ \dfrac{1}{\sqrt{2}} \left[\alpha(1)\beta(2) - \alpha(2)\beta(1) \right] \right\}$

- Two electrons can be assigned to four spinorbitals in six ways, excited state determinants

- In configuration interaction (CI), a linear combination of electron configurations is used as a trial function

- CI gives the correct dissocation limit of H_2

General CI

Configuration state functions

- In a basis set of N_o members, there are N_o molecular orbitals
- In the ground state wavefunction, $\Psi = ||\phi_a \phi_b \dots \phi_l \phi_m \phi_n \dots \phi_z||$

  - the lowest $\dfrac{1}{2} N_e$ molecular orbitals (two electrons per orbital) are occupied

  - there are $N_o - \dfrac{1}{2} N_e$ unoccupied virtual orbitals

- In addition to the ground state wavefunction, excited states are possible
  - A singly excited determinant $\Psi_m^p = ||\phi_a \phi_b \dots \phi_l \phi_n \dots \phi_p \dots \phi_z||$ has an electron promoted from occupied spinorbital m to unoccupied spinorbital p
  - A doubly excited determinant $\Psi_{mn}^{pq} = ||\phi_a \phi_b \dots \phi_l \phi_o \dots \phi_p \dots \phi_q \dots \phi_z||$ has two electron promoted from occupied spinorbitals m and n to unoccupied spinorbital p and q
  - There are other multiply excited determinants

Configuration Interaction

- The exact ground-state wavefunction can be expressed as a linear combination of all possible N_e-electron Slater determinants,

$$\Psi = c_o \Psi_o + \sum_{a,p} c_a^p \Psi_a^p + \sum_{a<b,p<q} c_{ab}^{pq} \Psi_{ab}^{pq} + + \sum_{a<b<c,p<q<r} c_{abc}^{pqr} \Psi_{abc}^{pqr} + \dots,$$

where cs are expansion coefficients

- When this is used as a trial function, the method is known as full CI. Computationally expensive "gold standard"
- Difference between CI and HF is known as *correlation energy*
- Empirically, doubly excited states found to make large contribution to energy, inspiring configuration interaction doubles (CID)
- Including singly excited configurations does not add much cost, inspiring configuration interaction singles and doubles (CISD)

Moller-Plesset Perturbation Theory

Towards MPPT

- Perturbation theory
  - Alternative approach to correlation energy
  - Applicable when $\hat{\mathbf{H}} = \hat{\mathbf{H}}^{(0)} + \hat{\mathbf{H}}^{(1)}$ describes the Hamiltonian
    - $\hat{\mathbf{H}}^{(0)}$ is a Hamiltonian with a solvable Schrodinger equation
    - $\hat{\mathbf{H}}^{(1)}$ is a perturbation to this Hamiltonian
  - **Not** variational
- Many-Body Perturbation Theory - perturbation theory applied to many interacting particles
- Moller-Plesset Perturbation Theory (1934) - $\hat{\mathbf{H}}^{(0)}$ is the Fock operator

The Perturbation

$$\hat{\mathbf{H}}^{(1)} = \hat{\mathbf{H}} - \hat{\mathbf{H}}^{(0)}$$

$$= \left[-\frac{1}{2} \sum_{i=1}^{2N} \nabla_i^2 - \sum_{i=1}^{2N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{2N} \sum_{j>i} \frac{1}{r_{ij}} + \sum_{A}^{M} \sum_{B<A}^{M} \frac{Z_A Z_B}{Z_{AB}} \right]$$

$$- \left[-\frac{1}{2} \sum_{i=1}^{2N} \nabla_i^2 - \sum_{i=1}^{2N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{2N} \sum_{j=1}^{N} \left(2J_j(r_i) - K_j(r_i) \right) \right]$$

$$= \sum_{i=1}^{2N} \left[\sum_{j>i} \frac{1}{r_{ij}} - \sum_{j=1}^{N} \left(2J_j(r_i) - K_j(r_i) \right) \right]$$

MPPT Energies

- $E_0^{(1)} = \left\langle \Psi_0 \middle| \hat{\mathbf{H}}^{(1)} \middle| \Psi_0 \right\rangle$ is first-order correction

- $E_0^{(2)} = \sum\limits_{j \neq 0} \dfrac{\left\langle \Psi_j \middle| \hat{\mathbf{H}}^{(1)} \middle| \Psi_0 \right\rangle \left\langle \Psi_0 \middle| \hat{\mathbf{H}}^{(1)} \middle| \Psi_j \right\rangle}{E_0^{(0)} - E_J^{(0)}}$ is second-order correction

- Hartree-Fock energy is the sum of the zero-order energy and first-order correction
- Inclusion of second-order correction is known as **MP2**
- MP3 and MP4 also exist. MP4 ~20x more time than HF.

Density Functional Theory

Wave function versus electron density

- So far, everything has been based on a wave function.
- For a one-electron operator $\hat{\mathbf{A}}(x, y, z)$, the expectation value is,

$$\left\langle \Psi \left| \hat{\mathbf{A}} \right| \Psi \right\rangle = \int\int\int \Psi^*(x, y, z) A(x, y, z) \Psi(x, y, z) \, dx dy dz$$

$$= \int\int\int A(x, y, z) \rho(x, y, z) \, dx dy dz, \text{ where } \rho(x, y, z) = \Psi^*(x, y, z) \Psi(x, y, z)$$

- This electron density is conceptually simpler and experimentally measurable (X-ray diffraction)
- It is sufficient for one-electron operators, but the Hamiltonian also includes two-electron operators

Density functional theory

- In 1964, Pierre Hohenberg and Walter Kohn proved
  - an existence theorem: $E = E[\rho]$, that the ground-state energy is a *functional* of the electron density

  - A functional maps a function to a number, e.g. $I[f] = \int_1^2 f(x)dx$

  - proved existence of functional but *does not* specify what it is
- a variation theorem: $E_o = E[\rho_o] \leq E[\rho]$, for a trial density ρ

More on DFT

- Comparison of approach to Hartree-Fock
  - Kohn-Sham DFT replaces the many-body problem of interacting electrons in a static external potential with non-interacting electrons moving in an *effective* potential
  - The effective potential includes the external potential and Coulomb effects of exchange and correlation interactions
- Speed of DFT comparable to HF, and accuracy comparable to post-HF
- No *ab initio* because exact energy functional unknown
- Much work in DFT is related to finding better functionals. One popular one is by Becke, Lee, Yang, and Parr (BLYP)
- DFT combines a functional with a basis set, eg. BLYP/6-31G*

Review Questions

- What is the expected energy when atoms in a molecule are separated by a large distance?

- In configuration interaction, what are the configurations that are interacting?

- In Moller-Plesset perturbation theory, what is the reference state?

- What is a functional?

- What type of density does density functional theory refer to?

- Of configuration interaction, Moller-Plesset perturbation theory, and density functional theory, which use variation theorems?