

Electronic Structure Theory

Lecture Schedule



1. Born-Oppenheimer approx.- energy surfaces
2. **Mean-field (Hartree-Fock) theory- orbitals**
3. Pros and cons of HF- RHF, UHF
4. Beyond HF- why?
5. First, one usually does HF-how?
6. Basis sets and notations
7. MPn, MCSCF, CI, CC, DFT
8. Gradients and Hessians
9. Special topics: accuracy, metastable states

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To whom are these lectures directed?

Ph. D. level students who have completed first-year graduate classes in quantum mechanics in a chemistry or physics department and who wish to learn more about electronic structures.

Research-active experimental chemists who have at least this same background and who are presently or wish to use electronic structure calculations to help interpret and guide their scientific studies.

Ph. D. and postdoctoral students specializing in **theoretical chemistry** but with emphasis outside electronic structure theory can also benefit.

Faculty at **primarily undergraduate institutions** who wish to include more theory in their classes and who have had sufficient background.

Sources of additional information- beyond the tip of the iceberg.

Molecular Electronic Structure Theory, Helgaker, Jørgensen, Olsen

Second Quantization Based Methods in Quantum Chemistry,
Jørgensen, Simons

Quantum Mechanics in Chemistry, Simons, Nichols (http://simons.hec.utah.edu/TheoryPage/quantum_mechanics_in_chemi.htm)

My theoretical chemistry web site: <http://simons.hec.utah.edu/TheoryPage>

An Introduction to Theoretical Chemistry, Simons (<http://simons.hec.utah.edu/NewUndergradBook/>)

Quantum Chemistry, 5th Ed., I. N. Levine

Lecture Schedule:

Session 1: Born-Oppenheimer approximation: adiabatic and diabatic surfaces; non-BO couplings; surface crossings; the electronic and vibration-rotation Schrödinger equations; minima and transition states.

Session 2: Hartree-Fock: atomic units; electron-nuclear and electron-electron cusps, antisymmetry; Coulomb holes, mean-field potential, Slater determinants, spin-orbitals, spin functions, Slater-Condon rules, The HF equations, Coulomb and exchange, Koopmans' theorem, orbital energies, problems arising when using single determinant approximations; certain states require more than one determinant; restricted and unrestricted wave functions.

Session 3: Pros and cons of HF: limitations of single determinants, configuration state functions, homolytic bond cleavage and the need for CI, dynamical and essential electron correlation; restricted and unrestricted HF (RHF, UHF),

Session 4: Beyond HF-Why? Bond breaking, configuration mixing, polarized orbital pairs for essential and dynamical correlation, how important correlation is; reminder about cusps and introduction to explicitly correlated wave functions.

Session 5: First, one usually does HF-how? LCAO-MO, scaling with basis size, SCF process, how to start the SCF, meaning of occupied and virtual orbitals, spin problems in UHF,
Basis notations; complete-basis extrapolation of the Hartree-Fock and correlation energies.

Session 6: Basis sets and notations ; STOs and GTOs, nuclear cusps, contracted GTOs, core, valence, polarization, diffuse, and Rydberg basis functions, notations, complete basis extrapolation, basis set superposition errors (BSSE).

Session 7: Why beyond HF?MPn, MCSCF, CI, CC, DFT. MP theory, E^1 , E^2 , ψ^1 , Brillouin theorem, divergence and why, size-extensivity, multi-configuration SCF (MCSCF), AO-to-MO integral transformation, configuration interaction (CI)); coupled-cluster (CC), density functional theory (DFT), Kohn-Sham equations, strengths and weaknesses, scaling with basis size.

Session 8: Gradients, Hessians, minima and transition states, reaction paths, harmonic vibrational frequencies, Hellmann-Feynman theorem, orbital responses.

Session 9: Typical error magnitudes for various methods and various basis sets. Special tricks for studying metastable anions; variational collapse; virtual orbitals are difficult to identify- examples; long-range potentials and the centrifugal potential; valence and long-range components of the wave function; relation to electron scattering; charge stabilization method; the stabilization method.

Some of the material will be covered in problem/discussion sections.

The following several slides contain **material I ask you to read and refresh your memory about prior to the School**. I am asking you to do so because the electronic structure lectures are the first you will hear at the School, and I would like you to prepare beforehand. During the School, we will provide you with material from the other Lecturers that you can view prior to those lectures to similarly prepare.

You should have had this material in your quantum, spectroscopy, or angular momentum classes. If there is something you don't know about, please have a friend teach you so you will be versed in it when the School begins. I. N. Levine's text *Quantum Chemistry* 5th Ed. contains much of this material (look under ladder operators, angular momentum, spin, Slater determinants, and Condon-Slater rules).

A brief refresher on **spin**

$$S_z \alpha = 1/2 \hbar \alpha$$

$$S_z \beta = -1/2 \hbar \beta$$

$$S^2 \alpha = \hbar^2 1/2(1/2 + 1) \alpha = 3/4 \hbar^2 \alpha$$

$$S^2 \beta = \hbar^2 1/2(1/2 + 1) \beta = 3/4 \hbar^2 \beta$$

Special case of

$$J^2 |j, m\rangle = \hbar^2 j(j+1) |j, m\rangle$$

$$\langle \alpha | \alpha \rangle = 1$$

$$\langle \alpha | \beta \rangle = 0$$

$$\langle \beta | \beta \rangle = 1$$

$$S_- \alpha = \hbar \sqrt{\frac{1}{2}(\frac{1}{2} + 1) - \frac{1}{2}(\frac{1}{2} - 1)} \beta = \hbar \beta$$

$$S_- \beta = 0$$

Special case of

$$J_{\pm} |j, m\rangle = \hbar \sqrt{j(j+1) - m(m \pm 1)} |j, m \pm 1\rangle$$

For acting on a product of spin-orbitals, one uses

$$S_z = \sum_j S_z(j) \quad S_- = \sum_j S_-(j) \quad S^2 = S_- S_+ + S_z^2 + \hbar S_z$$

Examples: $S_z \alpha(1)\alpha(2) = 1/2 \hbar \alpha(1)\alpha(2) + 1/2 \hbar \alpha(1)\alpha(2) = \hbar \alpha(1)\alpha(2)$

$$S_- \alpha(1)\alpha(2) = \hbar \beta(1)\alpha(2) + \hbar \alpha(1)\beta(2)$$

Let's practice **forming triplet and singlet spin** functions for 2 e's.

We always begin with the highest M_S function because it is "pure".

$$\alpha(1)\alpha(2)$$

So, $M_S = 1$; has to be **triplet**

$$S_z \alpha(1)\alpha(2) = 1/2\hbar\alpha(1)\alpha(2) + 1/2\hbar\alpha(1)\alpha(2) = \hbar\alpha(1)\alpha(2)$$

$$S_z \beta(1)\beta(2) = -1/2\hbar\beta(1)\beta(2) - 1/2\hbar\beta(1)\beta(2) = -\hbar\beta(1)\beta(2)$$

So, $M_S = -1$; has to be **triplet**

$$S_- \alpha(1)\alpha(2) = \hbar\beta(1)\alpha(2) + \hbar\alpha(1)\beta(2)$$

$$= \hbar\sqrt{1(1+1) - 1(1-1)} |S = 1, M_S = 0\rangle$$

$$\text{So, } |1,0\rangle = \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

This is the $M_S = 0$ **triplet**

How do we get the singlet? It has to have $M_S = 0$ and be orthogonal to the $M_S = 0$ triplet. So, **the singlet** is

$$|0,0\rangle = \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

Slater determinants ($P_{i,j}$) in several notations. First, for two electrons.

$$\begin{aligned}\psi(r_1, r_2) &= \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_\alpha(r_1) & \varphi_\beta(r_1) \\ \varphi_\alpha(r_2) & \varphi_\beta(r_2) \end{vmatrix} \\ &= \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi(r_1)\alpha(1) & \varphi(r_1)\beta(1) \\ \varphi(r_2)\alpha(2) & \varphi(r_2)\beta(2) \end{vmatrix}\end{aligned}$$

Shorthand

$$\psi(r_1, r_2) = |\varphi_\alpha \varphi_\beta|$$

$$\begin{aligned}\psi(r_1, r_2) &= \frac{1}{\sqrt{2}} (\varphi(r_1)\alpha(1)\varphi(r_2)\beta(2) - \varphi(r_1)\beta(1)\varphi(r_2)\alpha(2)) \\ &= \varphi(r_1)\varphi_2(r_2) \frac{1}{\sqrt{2}} \{ \alpha(1)\beta(2) - \beta(1)\alpha(2) \}\end{aligned}$$

Symmetric space;
antisymmetric spin
(**singlet**)

$$|\phi_1\alpha\phi_2\alpha| = \frac{1}{\sqrt{2}} [\phi_1\alpha(1)\phi_2\alpha(2) - \phi_1\alpha(2)\phi_2\alpha(1)] = \frac{1}{\sqrt{2}} [\phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2)]\alpha(1)\alpha(2)$$

Antisymmetric space; symmetric spin (**triplet**)

$$\psi(r_1, r_2) = -\psi(r_2, r_1)$$

$$\frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_\alpha(r_1) & \varphi_\beta(r_1) \\ \varphi_\alpha(r_2) & \varphi_\beta(r_2) \end{vmatrix} = -\frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_\alpha(r_2) & \varphi_\beta(r_2) \\ \varphi_\alpha(r_1) & \varphi_\beta(r_1) \end{vmatrix}$$

Notice the $P_{i,j}$
antisymmetry

More practice with Slater determinants

$$\psi(r_1, r_2, \dots, r_n) = \left| \varphi_{1\alpha}, \varphi_{2\alpha}, \dots, \varphi_{n\beta} \right| \quad \text{Shorthand notation for general case}$$

$$\psi(r_1, r_2, \dots, r_n) = \begin{vmatrix} \varphi_{1\alpha}(1) & \varphi_{2\alpha}(1) & \dots & \varphi_{n\beta}(1) \\ \varphi_{1\alpha}(2) & \varphi_{2\alpha}(2) & \dots & \varphi_{n\beta}(2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_{1\alpha}(n) & \varphi_{2\alpha}(n) & \dots & \varphi_{n\beta}(n) \end{vmatrix} \quad \text{Odd under interchange of any two rows or columns}$$

$$\psi(r_1, r_2, \dots, r_n) =$$

$$\frac{1}{\sqrt{n!}} \sum_P (-1)^{p(P)} P \{ \varphi_{1\alpha}(1) \varphi_{2\alpha}(2) \dots \varphi_{n\beta}(n) \} = O \{ \varphi_{1\alpha} \varphi_{2\alpha} \dots \varphi_{n\beta} \}$$

P permutation operator

$$(-1)^{p(P)}$$

parity ($p(P)$ least number of transpositions that brings the indices back to original order)

$$O = \frac{1}{\sqrt{n!}} \sum_P (-1)^{p(P)} P \quad \text{antisymmetrizer}$$

The dfn. of the Slater determinant contains a $N^{-1/2}$ normalization.

Example : Determinant for 3-electron system

$$\begin{aligned}
 O\{\varphi_1 \varphi_2 \varphi_3\} &= \frac{1}{\sqrt{6}} \left(1 - \sum_{i,j} P_{ij} + \sum_{i,j,k} P_{ijk} \right) \{\varphi_1 \varphi_2 \varphi_3\} \\
 &= \frac{1}{\sqrt{6}} \left\{ \begin{aligned} &\varphi_1(1)\varphi_2(2)\varphi_3(3) - \varphi_2(1)\varphi_1(2)\varphi_3(3) \\ &-\varphi_3(1)\varphi_2(2)\varphi_1(3) - \varphi_1(1)\varphi_3(2)\varphi_2(3) \\ &+\varphi_2(1)\varphi_3(2)\varphi_1(3) + \varphi_3(1)\varphi_1(2)\varphi_2(3) \end{aligned} \right\}
 \end{aligned}$$

permutations	1,	P_{12} ,	P_{13} ,	P_{23} ,	P_{231} ,	P_{312}
transpositions	0	1	3	1	2	2
parity	+	-	-	-	+	+

The good news is that one does not have to deal with most of these complications. Consider two Slater determinants (SD).

$$\psi_A = \frac{1}{\sqrt{N!}} \sum_P (-1)^{P^p} P \varphi_1(1) \varphi_2(2) \varphi_3(3) \dots \varphi_N(N)$$

$$\psi_B = \frac{1}{\sqrt{N!}} \sum_Q (-1)^{Q^q} Q \varphi'_1(1) \varphi'_2(2) \varphi'_3(3) \dots \varphi'_N(N)$$

Assume that you have taken t permutations¹ to bring the two SDs into maximal coincidence. Now, consider evaluating the integral

$$\int d1d2d3\dots dN \psi_A^* \left[\sum_{j=1,N} f(j) + \sum_{j < k=1,N} g(i,j) \right] \psi_B$$

where $f(i)$ is any one-electron operator (e.g., $-Z_A/|\mathbf{r}_j - \mathbf{R}_A|$) and $g(i,j)$ is any two-electron operator (e.g., $1/|\mathbf{r}_j - \mathbf{r}_k|$). This looks like a horrible task ($N! \times (N + N^2) \times N!$ terms).

1. A factor of $(-1)^t$ will then multiply the final integral I

$$I = \int d1d2d3\dots dN \psi_A^* \left[\sum_{j=1,N} f(j) + \sum_{j<k=1,N} g(i,j) \right] \psi_B$$

$$\psi_A = \frac{1}{\sqrt{N!}} \sum_P (-1)^{p^P} P \varphi_1(1) \varphi_2(2) \varphi_3(3) \dots \varphi_N(N)$$

$$\psi_B = \frac{1}{\sqrt{N!}} \sum_Q (-1)^{q^Q} Q \varphi'_1(1) \varphi'_2(2) \varphi'_3(3) \dots \varphi'_N(N)$$

1. The permutation P commutes with the f + g sums, so

$$I = \frac{1}{\sqrt{N!}} \int d\tau \sum_P (-1)^{p^P} \varphi^*_{1}(1) \varphi^*_{2}(2) \varphi^*_{3}(3) \dots \varphi^*_{N}(N) \left[\sum_{j=1,N} f(j) + \sum_{j<k=1,N} g(i,j) \right] P \psi_B$$

2. $P \psi_B = (-1)^{p^P} \psi_B$ and $\sum_P (-1)^{p^P} (-1)^{p^P} = N!$ so

$$\begin{aligned} I &= \frac{N!}{\sqrt{N!}} \int d\tau \sum_P \varphi^*_{1}(1) \varphi^*_{2}(2) \varphi^*_{3}(3) \dots \varphi^*_{N}(N) \left[\sum_{j=1,N} f(j) + \sum_{j<k=1,N} g(i,j) \right] \psi_B \\ &= \int d\tau \varphi^*_{1}(1) \varphi^*_{2}(2) \varphi^*_{3}(3) \dots \varphi^*_{N}(N) \left[\sum_{j=1,N} f(j) + \sum_{j<k=1,N} g(i,j) \right] \sum_Q (-1)^{q^Q} Q \varphi'_1(1) \varphi'_2(2) \varphi'_3(3) \dots \varphi'_N(N) \end{aligned}$$

Now what?

$$I = \int d\tau \varphi_{*1}^*(1) \varphi_{*2}^*(2) \varphi_{*3}^*(3) \dots \varphi_{*N}^*(N) \left[\sum_{j=1, N} f(j) + \sum_{j < k=1, N} g(i, j) \right] \sum_Q (-1)^{q_Q} Q \varphi'_{*1}(1) \varphi'_{*2}(2) \varphi'_{*3}(3) \dots \varphi'_{*N}(N)$$

Four cases: the **Slater-Condon rules** (memorize them)

ψ_A and ψ_B differ by three or more spin-orbitals: $I = 0$

ψ_A and ψ_B differ by two spin-orbitals- $\phi_{Ak} \phi_{Al}; \phi_{Bk} \phi_{Bl}$

$$I = \int dk dl \varphi_{*Ak}^*(k) \varphi_{*Al}^*(l) g(k, l) [\varphi_{Bk}(k) \varphi_{Bl}(l) - \varphi_{Bl}(k) \varphi_{Bk}(l)]$$

ψ_A and ψ_B differ by one spin-orbital- $\phi_{Ak}; \phi_{Bk}$

$$I = \sum_{j \in A, B} \int dk dj \varphi_{*Ak}^*(k) \varphi_{*j}^*(j) g(k, j) [\varphi_{Bk}(k) \varphi_j(j) - \varphi_j(k) \varphi_{Bk}(j)] \\ + \int dk \varphi_{*Ak}^*(k) f(k) \varphi_{Bk}(k)$$

ψ_A and ψ_B are identical

$$I = \sum_{k < j \in A} \int dk dj \varphi_{*k}^*(k) \varphi_{*j}^*(j) g(k, j) [\varphi_k(k) \varphi_j(j) - \varphi_j(k) \varphi_k(j)] \\ + \sum_{k \in A} \int dk \varphi_{*k}^*(k) f(k) \varphi_k(k)$$