

PROJECT: Testing the Transferability of Integrals in Multiplet-Sum (MS) Density-Functional Theory (DFT)

You will learn



to run a quantum chemistry program (deMon2k)

about some of the limitations of DFT and how to overcome them

that research need not require heavy or expensive calculations provided that you have a good formal understanding

Mark E. Casida (櫻田 マーク , 卡西达 马克)

Professeur, chimie théorique

Laboratoire de Spectrométrie, Interactions et Chimie Théorique (SITh)

Département de Chimie Moléculaire (DCM, UMR CNRS/UGA 5250)

Institut de Chimie Moléculaire de Grenoble (ICMG, FR-2607)

Université Grenoble Alpes (UGA)

301 rue de la Chimie

CS 40700

38058 Grenoble cedex 9

France

e-mail: mark.casida@univ-grenoble-alpes.fr

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Kohn-Sham DFT replaces the real interacting system with a fictitious system of noninteracting electrons, described by a single-determinantal (SD) wavefunction (i.e., the Kohn-Sham determinant serves as the reference wavefunction for DFT).

Fortunately a SD reference is appropriate for the ground state of most closed-shell molecules near their equilibrium geometry.

Unfortunately a SD reference needs to be replaced with a reference multideterminantal (MD) wavefunction when (symmetry) degenerate (or quasidegenerate) states are present.

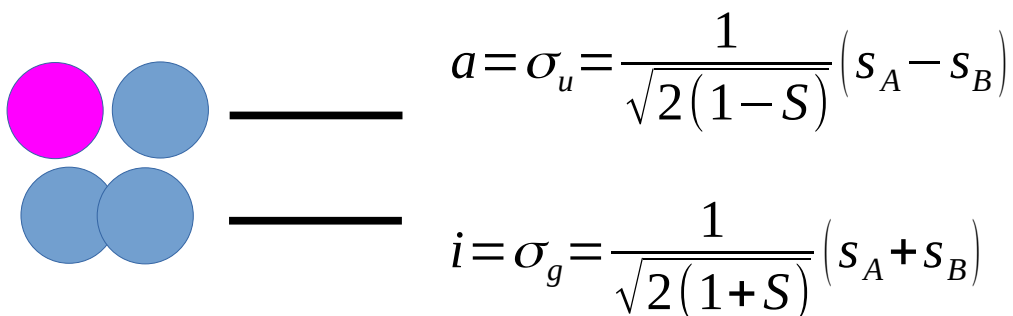
Wavefunction theory (WFT)

$$\Psi = \Phi + \sum_{i,a} \Phi_i^a C_i^a + \sum_{i,j}^{a,b} \Phi_{i,j}^{a,b} C_{i,j}^{a,b} + \dots$$

We speak of *dynamical correlation* when Φ is a SD and WFT requires millions (billions) of correction terms for chemical accuracy. DFT beats WFT here when it comes to efficient calculations.

We speak of *static correlation* when the series diverges unless Φ is rechosen to be MD. This is where DFT typically fails and WFT is preferred.

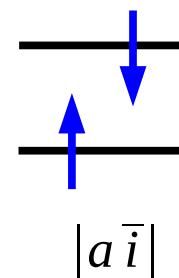
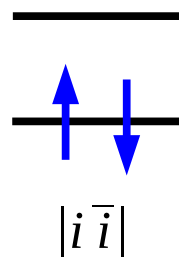
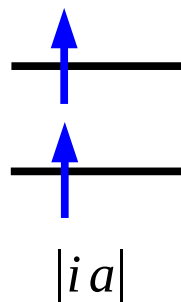
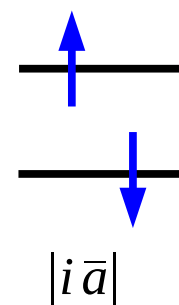
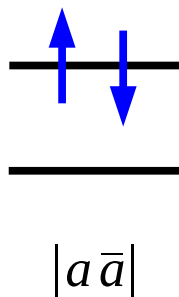
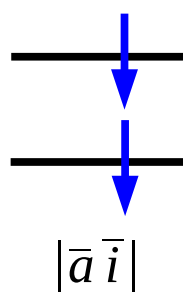
H₂ AS A SIMPLE EXAMPLE OF WHERE STATIC CORRELATION IS IMPORTANT



The overlap matrix $S = \langle s_A | s_B \rangle$

is used by chemists as one measure of bonding.

Possible fillings:



CONFIGURATION INTERACTION (CI)

Expanding $\Psi = |i\bar{i}\rangle C_0 + |a\bar{i}\rangle C_i^a + |i\bar{a}\rangle C_{\bar{i}}^{\bar{a}} + |ia\rangle C_{\bar{i}}^a + |a\bar{i}\rangle C_i^{\bar{a}} + |a\bar{i}\rangle C_{i\bar{i}}^{a\bar{a}}$

and using the variational principle, leads to the classic configuration interaction (CI) eigenvalue problem,

$$\begin{pmatrix} E[i\bar{i}] & 0 & 0 & 0 & 0 & B \\ 0 & E[a\bar{i}] & A & 0 & 0 & 0 \\ 0 & A & E[i\bar{a}] & 0 & 0 & 0 \\ 0 & 0 & 0 & E[ia] & 0 & 0 \\ 0 & 0 & 0 & 0 & E[\bar{a}\bar{i}] & 0 \\ B & 0 & 0 & 0 & 0 & E[a\bar{a}] \end{pmatrix} \begin{pmatrix} C_0 \\ C_i^a \\ C_{\bar{i}}^{\bar{a}} \\ C_{\bar{i}}^a \\ C_i^{\bar{a}} \\ C_{i\bar{i}}^{a\bar{a}} \end{pmatrix} = E \begin{pmatrix} C_0 \\ C_i^a \\ C_{\bar{i}}^{\bar{a}} \\ C_{\bar{i}}^a \\ C_i^{\bar{a}} \\ C_{i\bar{i}}^{a\bar{a}} \end{pmatrix}$$

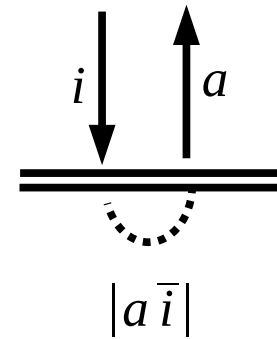
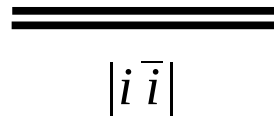
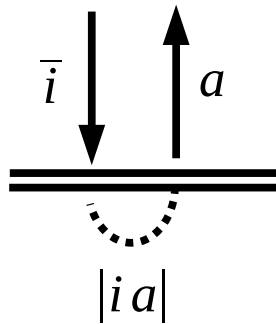
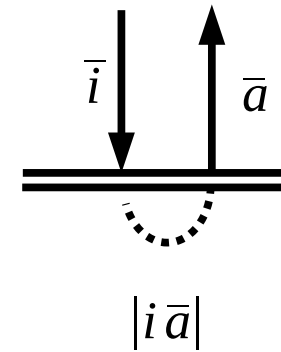
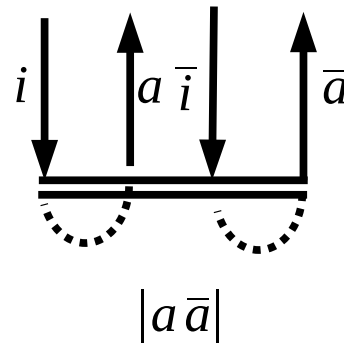
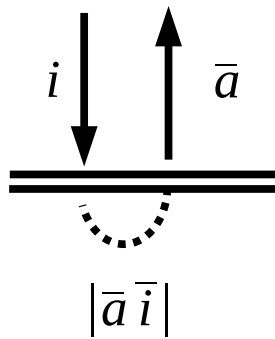
There are a lot of zeros because there is both spin and spatial symmetry in this problem.

As $E[i\bar{a}] = E[a\bar{i}]$, then it is easy to see that the block indicated in red diagonalizes

to give $E_{\pm} = E[a\bar{i}] \pm A$

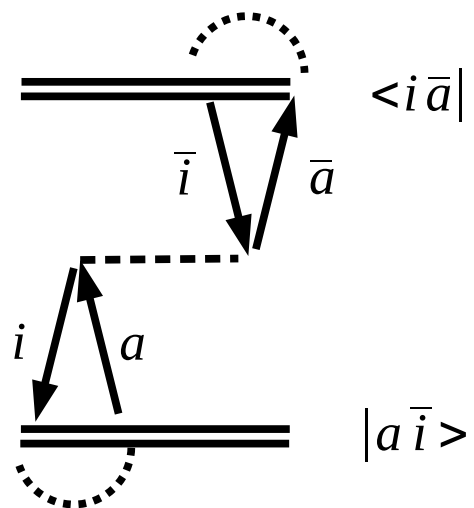
THE WFT LANGUAGE OF FEYNMAN DIAGRAMS

WFT Feynman diagrams are convenient for figuring out the A and B matrix elements.



WFT FORMULAE FOR THE A AND B INTEGRALS

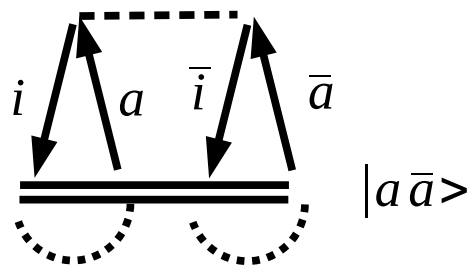
$$A = \langle a \bar{i} | \hat{H} | i \bar{a} \rangle = (ia || ia)$$



$$(pq || rs) = \int \int p^*(1) q(1) \frac{1}{r_{12}} r^*(2) s(2) d1 d2$$

$$= \langle i \bar{i} |$$

$$B = \langle i \bar{i} | \hat{H} | a \bar{a} \rangle = (ia || ia)$$



$$\begin{pmatrix} E[i\bar{i}] & 0 & 0 & 0 & 0 & B \\ 0 & E[a\bar{i}] & A & 0 & 0 & 0 \\ 0 & A & E[i\bar{a}] & 0 & 0 & 0 \\ 0 & 0 & 0 & E[ia] & 0 & 0 \\ 0 & 0 & 0 & 0 & E[\bar{a}\bar{i}] & 0 \\ B & 0 & 0 & 0 & 0 & E[a\bar{a}] \end{pmatrix} \begin{pmatrix} C_0 \\ C_i^a \\ C_{\bar{i}}^{\bar{a}} \\ C_{\bar{i}}^a \\ C_i^{\bar{a}} \\ C_{i\bar{i}}^{a\bar{a}} \end{pmatrix} = E \begin{pmatrix} C_0 \\ C_i^a \\ C_{\bar{i}}^{\bar{a}} \\ C_{\bar{i}}^a \\ C_i^{\bar{a}} \\ C_{i\bar{i}}^{a\bar{a}} \end{pmatrix}$$

Diagonalization of this block leads to one singlet and three degenerate triplet wavefunctions $\Psi_{S,M}$

$$\Psi_{0,0} = \frac{1}{\sqrt{2}} (|a\bar{i}| + |i\bar{a}|) \quad \text{open-shell singlet (higher energy)}$$

$$\Psi_{1,+1} = |ia|$$



$$\Psi_{1,0} = \frac{1}{\sqrt{2}} (|a\bar{i}| - |i\bar{a}|)$$

$$\Psi_{1,-1} = |\bar{i}\bar{a}|$$

degenerate triplets (lower energy)



IDEA!

-  Include dynamic correlation by using DFT to calculate the diagonal elements.
-  Include static correlation by using WFT to calculate the off-diagonal elements.

$$\begin{bmatrix} E[i\bar{i}] & 0 & 0 & 0 & 0 & B \\ 0 & E[a\bar{i}] & A & 0 & 0 & 0 \\ 0 & A & E[i\bar{a}] & 0 & 0 & 0 \\ 0 & 0 & 0 & E[i a] & 0 & 0 \\ 0 & 0 & 0 & 0 & E[\bar{a} \bar{i}] & 0 \\ B & 0 & 0 & 0 & 0 & E[a \bar{a}] \end{bmatrix} \begin{bmatrix} C_0 \\ C_i^a \\ C_{\bar{i}}^{\bar{a}} \\ C_{\bar{i}}^a \\ C_i^{\bar{a}} \\ C_{i\bar{i}}^{a\bar{a}} \end{bmatrix} = E \begin{bmatrix} C_0 \\ C_i^a \\ C_{\bar{i}}^{\bar{a}} \\ C_{\bar{i}}^a \\ C_i^{\bar{a}} \\ C_{i\bar{i}}^{a\bar{a}} \end{bmatrix}$$

Problem: The three triplet states are no longer degenerate!

$$\Psi_{0,0} = \frac{1}{\sqrt{2}} (|a \bar{i}| + |i \bar{a}|)$$

$$E_S = \langle \Psi_{0,0} | \hat{H} | \Psi_{0,0} \rangle = E[a \bar{i}] + A$$

$$\Psi_{1,+1} = |i a|$$

$$E_T = E[ia]$$

$$\Psi_{1,0} = \frac{1}{\sqrt{2}} (|a \bar{i}| + |i \bar{a}|)$$

$$E_T = \langle \Psi_{1,0} | \hat{H} | \Psi_{1,0} \rangle = E[a \bar{i}] - A$$

$$\Psi_{1,-1} = |\bar{i} \bar{a}|$$

Solving the three equations on the RHS gives

$$A = E[a \bar{i}] - E[ia] \neq (ai || ai) \quad (\text{except in WFT})$$

WHAT IF SYMMETRY ARGUMENTS ARE NOT ENOUGH?

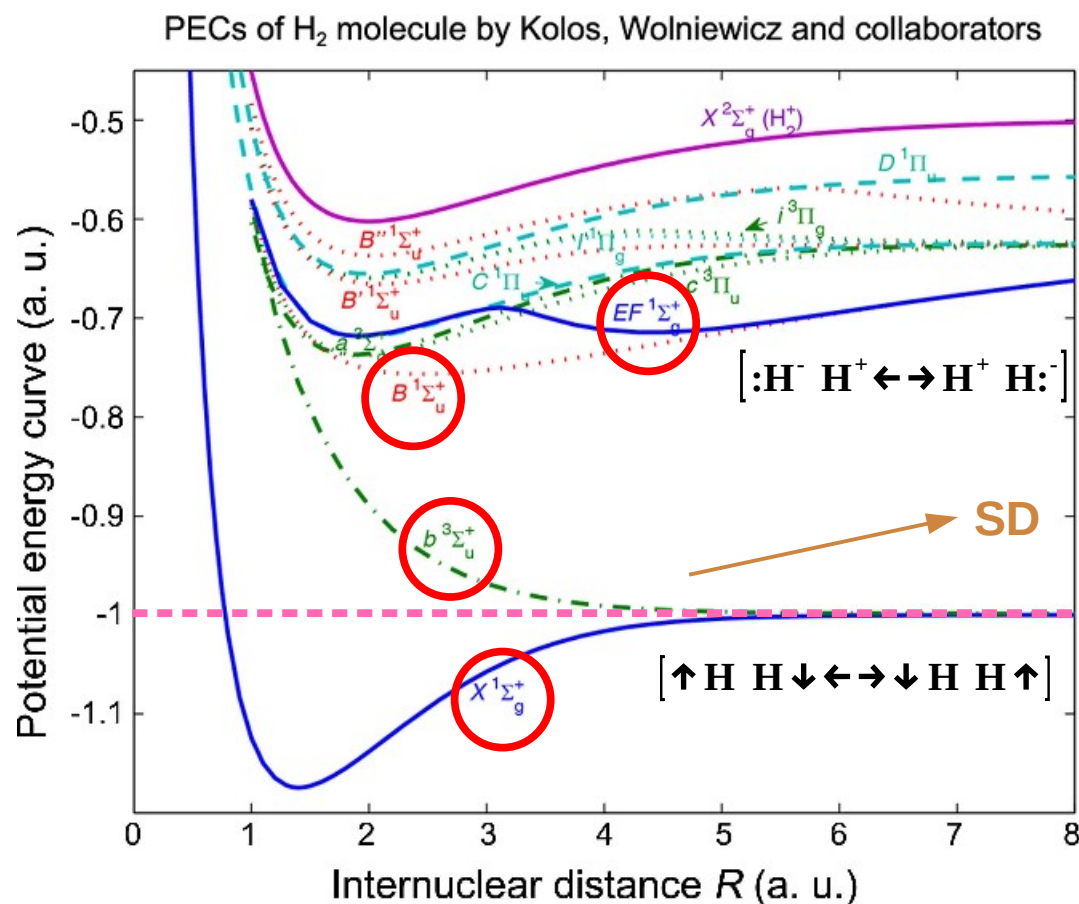


Figure 1. Potential energy curves of H₂ obtained by Kolos

Correct dissociation without symmetry breaking is obtained by solving

$$\begin{bmatrix} E[i\bar{i}] & B \\ B & E[a\bar{a}] \end{bmatrix} \begin{pmatrix} C_0 \\ C_{i\bar{i}}^{a\bar{a}} \end{pmatrix} = E \begin{pmatrix} C_0 \\ C_{i\bar{i}}^{a\bar{a}} \end{pmatrix}$$

What to use for B?

$$B = (ia || ia)$$

$$B = E[a\bar{i}] - E[ia]$$



WHAT WILL YOU GAIN IN DOING THIS PROJECT?



Extension to O_2 if time permits.



Additional explanation in tomorrow's special topics seminar.



Familiarity with quantum chemical methods.



Experience dealing with static correlation.



Possibility of contributing to research in progress.



Expansion of your network of Pan-African friends.

