

09-09-19_AESCM_lesson-04

September 10, 2019

1 AESCM lesson 04 (continuation of 02)

- Hour: 4
- Professor: Coen de Graff

1.1 Continuing CASPT2

1.1.1 Wrapping up some key points

- CCSD(T) and DFT are very powerful methods to do chemistry! BUT
- A single determinant is not always a reliable starting point (single reference methods, so HF is usually a nice start)
- Avoid bias by simultaneous optimization of CI expansion and orbital coefficients
- CASSCF lets us construct the MC wave functions in terms of orbitals
- Accurate calculations require to go beyond CASSCF
- CASPT2 is very successful, but you have to keep an eye on intruder states (-0.15 eV accuracy in E_{abs})
- NEVPT2 is an interesting alternative! (whatever it is :D)

1.2 Spin functions

It turns out that the usual arrow-up/arrow-down representation of a singlet is not a very good one.

$$\Phi = |\phi_1 \bar{\phi}_2|$$

$$[\hat{S}_z, \hat{S}^2] = 0 \quad [\hat{S}_z, \hat{S}^2] = 0 \quad [\hat{S}_z, \hat{S}^2] = 0$$

Complete these equations!!!! :((((

What is the proper eigenfunction of the open shell singlet?

Spin functions by genealogical approach: 1. Start with $N=1$ $\Psi(N-1) - \alpha(1)$ 2. Couple the second electron in parallel with the *add* formula 3. Couple the second electron in antiparallel with the *subtract* formula

If $\langle \phi_1 | \phi_2 \rangle = 1$

If $\langle \phi_1 | \phi_2 \rangle = 0$

We should be wary of spin contamination: mixings of singlets, triplets... which should not happen in our non relativistic work.

1.3 Spin-orbit coupling

It's a relativistic effect that is not considered in Schrödinger's equation (although it is in Dirac's).

Is it important in a non relativistic world?

Taking a cation-ligand system, it's responsible for: - Splitting the degenerate M_s levels - Mixing the spin eigenfunctions

Well... Dirac's equation is pretty fucking complicated. <:)

It has some off-diagonal terms that connect small and large components. Can we find a unitary transformation that decouples them? Yup! It's the Foldy-Wouthuysen transformation, which is the basis for the Douglas-Kroll-Hess (DKH) Hamiltonian.

How to introduce the spin-orbit coupling in a one-component approach?

1. Ground state and as many excited states as possible
2. Apply the perturbation equation (outdated woohooops)
3. It's better to construct the spin-orbit interaction matrix and diagonalise for E_i^{SO} , Ψ_i^{SO} (diagonal matrix elements: CASPT2 energies, off-diagonal matrix elements: spin-orbit interactions)

Case study: heptacoordinated Ni^{II} complex

1. aaaaa
2. Spin-orbit coupling (diagonalization of 45x45 matrix, getting 45 energies and 45 wave functions)
3. aaaaa

1.4 Alternatives to CASSCF

CASSCF has a maximum of 18 active orbitals and is prone to "configurational deadwood".

1.4.1 Restricted Active Space SCF (RASSCF)

- Easily doubles the active space
- Convergence is more problematic
- Generalized by GASSCF

1.4.2 Density Matrix Renormalization Group (DMRG)

First: renormalization theory

CHAIN OF ISING SPINS WHAT AAAAAAAAAAAAAA

Random notes - Same energy, different wavefunctions: degenerate states