

Excited states

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NOTE: In preparation of the following slides, I have made heavy use of the material presented by Björn Roos and Luis Serrano-Andrés at the Molcas workshop in València, Spain, 2006-04-20 – 26.

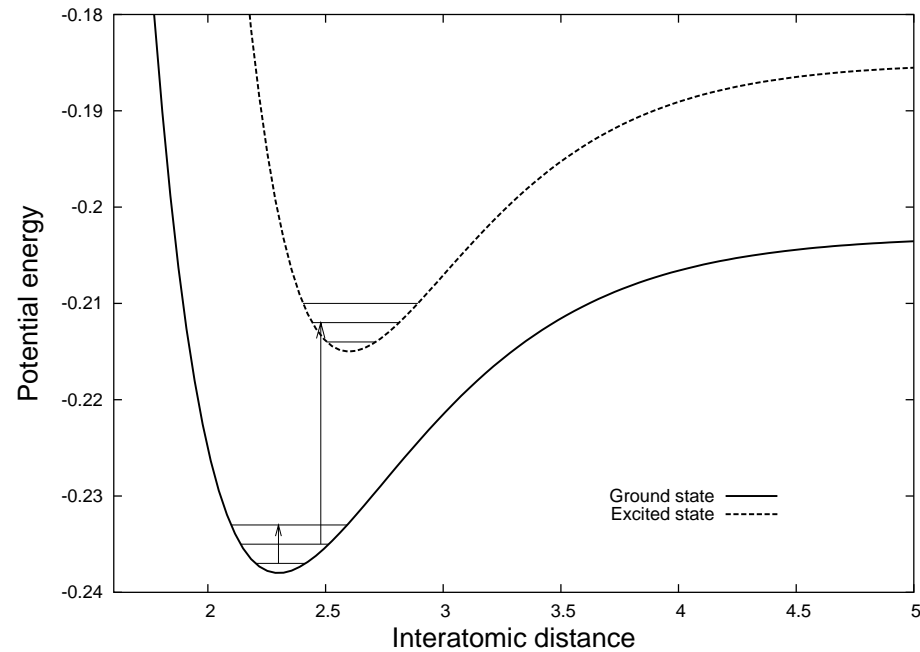
Excited states: Uses, purposes

- Spectroscopy.
- Photophysics.
- Photochemistry.

Quantum chemical methods

- Calculating potential energy functions and transition probabilities.
- Dynamics: Minimum energy paths, crossings, conical intersections.

The concept of Potential Energy Surfaces



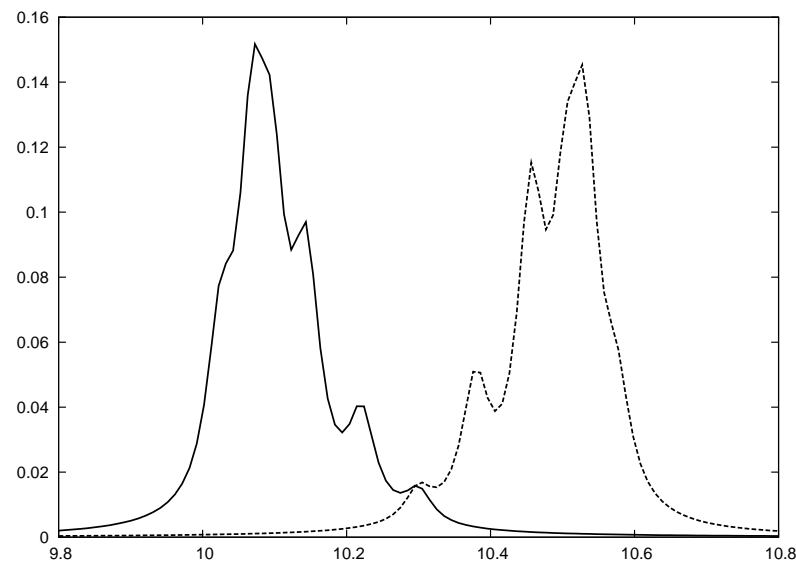
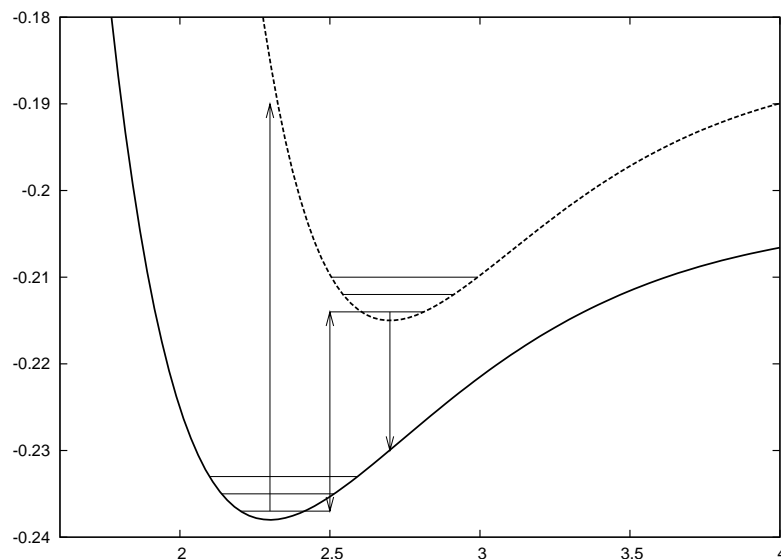
$$\hat{H}\Psi(R, r) = E\Psi(R, r) \quad \text{where } \hat{H} = \hat{T}^n + \hat{H}^e$$

$$\text{Ansatz: } \Psi(R, r) = \Phi^n(R)\Psi^e(r; R) \quad (\text{Born-Oppenheimer})$$

$$\hat{H}^e\Psi_i^e(r; R) = E_i^e\Psi_i^e(r; R)$$

$$(\hat{T}^n + E_i^e)\Phi_{ij}^n(R) = E_{ij}^n\Phi_{ij}^n(R)$$

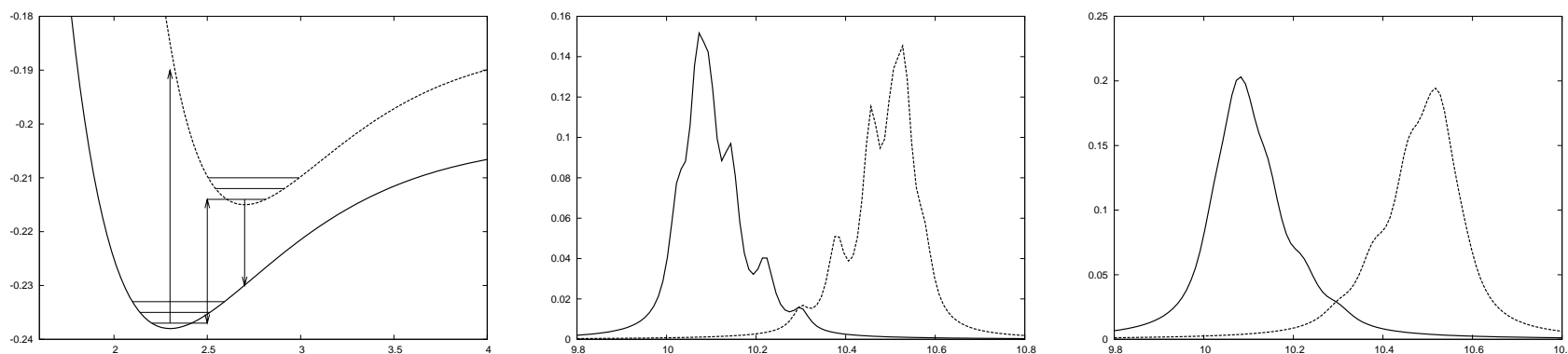
Measured spectrum vs computed PES



To the left, we see a ground and an excited PES, and transitions are indicated

- From the $v=0$ vibration level of the ground state up to vibration levels of the excited state.
- The 0-0 transition
- From the $v=0$ vibration level of the excited state down to vibration levels of the excited state.

Measured spectrum vs computed PES



The computed electronic transition energies are usually compared to accurate 0-0 transitions or approximate vertical transition energies measured from spectra. In the first case, they are corrected by zero-point vibration energies (ZPE's), usually in harmonic approximation:

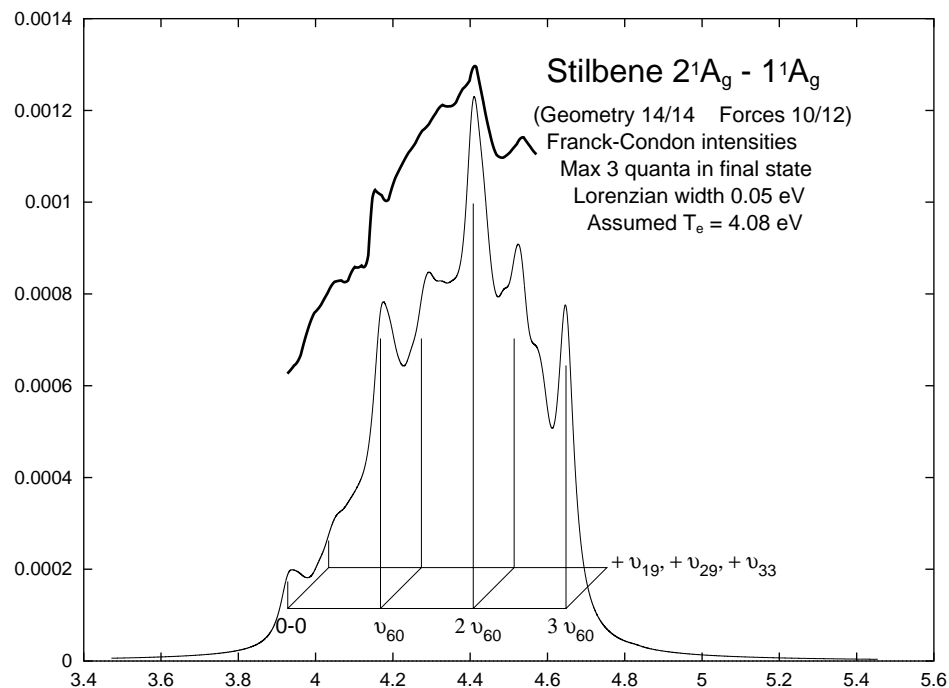
$$T_0 = T_e + \frac{1}{2} \sum_Q \omega_Q^i - \frac{1}{2} \sum_Q \omega_Q^f$$

(For small molecules, it also happens that T_e has been deduced by fitting a formula to the vibration lines).

In the second case, the experimental 'vertical' transition is often simply the peak position of a poorly resolved spectrum: Look out! The error could easily be 0.1 eV!

Measured spectrum vs computed PES

The best way to compare theoretically computed potential energy functions with experiments is to, either, compute the spectroscopic levels and then analyse them in precisely the same way that experimentalists do in order to extract spectroscopic parameters, or **even better: to 'construct' theoretical spectra that can be directly compared to experimental spectroscopic 'traces':**



This can be the only credible way to compare theory and experiment, if the spectrum is poorly resolved due to a large number of active vibrational modes. However, it requires calculated **intensities**.

The intensities of vibrational states

The intensities can be computed (in the dipole approximation) from the matrix elements of the dipole operator:

$$M_{gi,fj} = \left\langle \Psi_{gi}(R, r) \left| \sum_n Q_n R_n - \sum_k er_k \right| \Psi_{fi}(R, r) \right\rangle$$

which in the Born-Oppenheimer approximation becomes

$$M_{gi,fj} = \left\langle \Phi_{gi}^n(R) \left| M(R) \right| \Phi_{fj}^n(R) \right\rangle$$

$$\text{where } M(R) = \left\langle \Psi_g^e \left| \sum_n Q_n R_n - \sum_k er_k \right| \Psi_f^e \right\rangle$$

and can be expanded around some common geometry as

$$M_{gi,fj} = M(R_0) \left\langle \Phi_{gi}^n(R) \left| \Phi_{fj}^n(R) \right\rangle + \left(\frac{\partial M}{\partial R} \right) \left\langle \Phi_{gi}^n(R) \left| \Delta R \right| \Phi_{fj}^n(R) \right\rangle + \dots$$

(the Herzberg-Teller expansion).

Quantum chemistry methods

- Single-orbital methods (SCF): Hartree-Fock, DFT. Closed shell, or high-spin open shell. Excitation energies by RPA/TDDFT (response).
- Single-determinant based methods: Closed shell or high-spin open shell reference function. CIS, CISD, CCSD(T), ... (states), RPA, SOPPA, ... (response methods),
- Multi-determinant based methods: Any electronic structure. RASSCF, MRCI, MRPT, CASPT2, (MRCC), ...

Also: After, or together with, calculation of electronic states, tools are used for optimizing equilibrium and transition structures, to compute e.g. matrix elements, transition strengths, vibrational wave functions, etc.

Multireference methods

Basis functions: Optimized linear combinations of gaussian functions.

Orbitals: Optimized linear combinations basis functions.

Wave functions: Optimized linear combinations of determinant functions.

MCSCF: Both orbitals and CI coefficients are variationally optimized.

CASSCF: All configuration functions (spin coupled determinants) with inactive orbitals always occupied, but active orbitals populated in every way possible for given nr of electrons and given spin.

'On top' of the CASSCF wave function: MRCI, MRACPF, CASPT2, . . . to account for 'dynamic correlation'.

The basis set

The quality of the calculations begin with the basis set.

The STO-3G, 6-31G*, etc are optimized for uncorrelated calculations for ground state atoms. They are less accurate, but useful for less demanding calculations.

They allow comparison to a very large body of published work.

The cc-pVDZ, cc-pVTZ, etc, optimized with correlation methods for ground state atoms. Designed to allow extrapolation to infinite basis.

ANO bases are optimized with correlation energy for atoms in a variety of states and bonding situations. Some program packages cannot use the general contraction of ANOs. Good and flexible for all uses within the design scope. Can be more expensive.

Note in particular ANO-RCC: Designed to work well with Douglas-Kroll relativistic calculations. Tested, and with uniform performance, through the whole periodic table.

What about TDDFT?

Ideally, DFT should include all correlation effects, and TDDFT should then yield vertical excitation energies \Rightarrow PE surfaces. Of course, DFT is not ideal. But it is quite cheap, so it is tempting to try. **However, it seems to be unreliable:**

C₇₀ excitation energies, eV

G.E. Scuseria et al., J. Chem. Phys. **109**, 8218(1998)

State	LSDA	B3LYP	RPA	CIS	Exp
¹ E' ₁	1.87	2.22	3.48	3.67	1.9
³ E' ₁	1.74	1.77		2.16	1.4–1.6

21 molecules, varying states: Average dev 0.4 eV
J. Fabian et al., Theochem **594**, 41(2002)

L. Serrano-Andrés and M. Merchán, Theochem **729**, 109(2005)

C ₃ 1 ¹ Π _u	0.76 eV	Butadiene 1 ³ B _u	-0.96 eV
O ₃ 2 ¹ A ₁	5.55 eV	Hexatriene 1 ³ B _u	-1.29 eV
Butadiene 2 ¹ A _g	1.44 eV	Naphtalene 1 ³ B _{2u}	-0.95 eV

Improvements, e.g. KSDFIT/MRCI (Grimme).

The CASSCF method

Spin-independent symmetry-adapted molecular orbitals are used. Divide the occupied orbitals into:

Inactive orbitals	Always doubly occupied
Active orbitals	Varying occupation allowed

Include all electronic configurations that are consistent with the given overall number of electrons, spin and space symmetry.

Molecule	Active orbitals	Active electrons	Number of CSF's	
H ₂	σ_g, σ_u	2	2	
O ₃	π_1, π_2, π_3	4	4	
2 C ₂ H ₄	4 π	4	8	
C ₁₀ H ₁₀	10 π	10	4 396	(¹ A _g)
			7 360	(³ A _g)
UO ₂	12	14	70 880	(C _{2v})
UO ₂ ⁺	13	13	322 388	(C _{2v})

This is the Complete Active Space (CAS) wave function

The CASSCF method: Optimize the CI coefficients and the MO's for a CAS wave function.

The RASSCF method

Spin-independent symmetry-adapted molecular orbitals are used. Divide the

occupied orbitals into:

Inactive orbitals	Always doubly occupied
Ras1 orbitals	Max number of holes
Ras2 orbitals	Varying occupation allowed
Ras3 orbitals	Max number of electrons

This can be regarded as a CAS with the additional possibility to excite out of some doubly occupied orbitals and into some virtual orbitals.

- Closed Shell SCF (RAS1, RAS2, RAS3 empty).
- SDTQ...CI with a closed shell reference function (RAS2 empty).
- CASSCF (RAS1 and RAS3 empty).
- SDCI with a CASSCF reference (max two holes in RAS1 and max two electrons in RAS3).
- Polarization CI (max one hole in RAS1).
- Core excited states (max one electron in RAS3 – which is a core orbital!).

The CASPT2 method

The CASPT2 method solves the equation

$$(\hat{H}_0 - E_0)\Psi_1 = -(\hat{H}_1 - E_1)\Psi_0$$

where Ψ_1 , the first-order perturbation to the wave function, is expressed as a large number — typically 100 000–1 000 000 — of excitation amplitudes. The zeroth order Hamiltonian,

$$\hat{H}_0 = \hat{P}_0 \hat{F} \hat{P}_0 + \hat{P}_I \hat{F} \hat{P}_I$$

is not diagonal, but the equation is solved by an iterative method (PCG). Here, \hat{P}_0 and \hat{P}_I are projectors onto the reference function and the interacting space, respectively.

The energy is then obtained by **the Hylleraas functional**,

$$E_2^{\text{Var}}[\Psi_1] = 2 \langle \Psi_1 | \hat{H}_1 - E_1 | \Psi_0 \rangle + \langle \Psi_1 | \hat{H}_0 - E_0 | \Psi_1 \rangle.$$

This energy is correct through second order in errors in Ψ_1 . This is taken advantage of when using real or imaginary shifts to eliminate spurious **intruder states**.

The IPEA shift

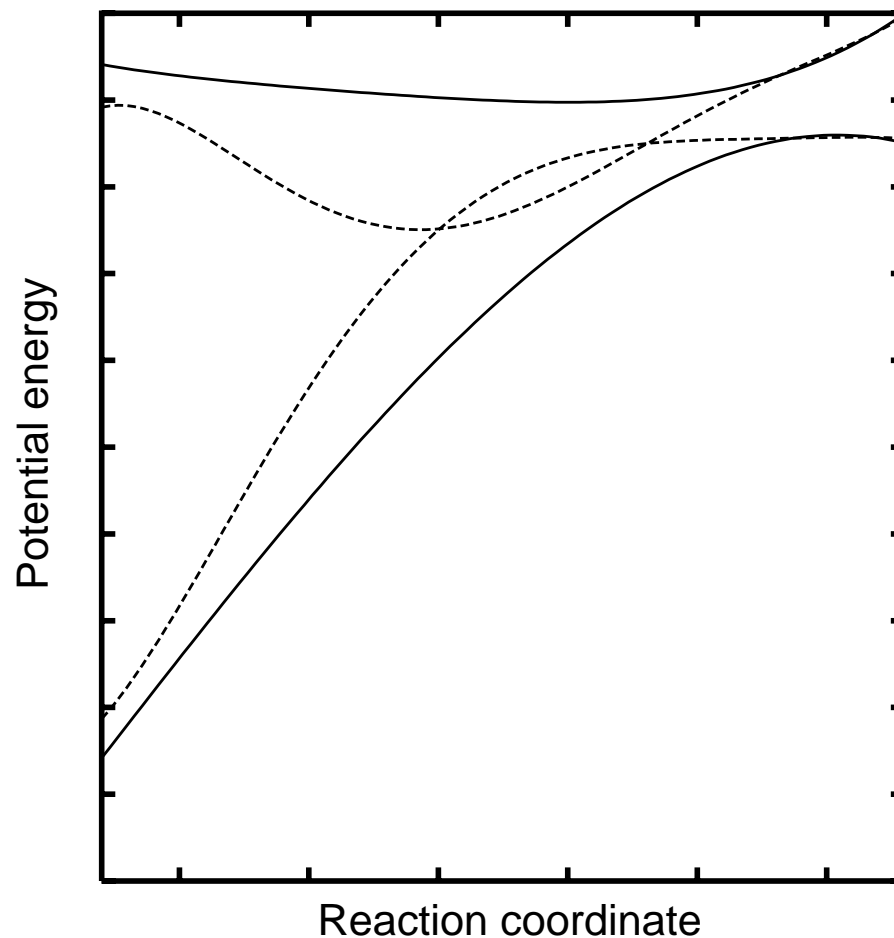
The Fock operator used in the definition of the zeroth order Hamiltonian is

$$\hat{F} = \sum_{pq} f_{pq} \hat{E}_{pq},$$
$$f_{pq} = h_{pq} + \sum_{rs} D_{rs} \left((pq|rs) - \frac{1}{2}(ps|rq) \right)$$

Such a one-electron operator does not distinguish between the situations when electrons are put into, or removed from, active orbitals. The new **IPEA shift** (by **Giovanni Ghigo**) remedies this, and has proven so generally advantageous that it is now the default choice from Molcas 6.4.

Multistate CASPT2

- Treats several states simultaneously at the CASPT2 level.
- Useful when there are states of the same symmetry close in energy.
- Compulsory for studying avoided crossings, conical intersections, etc.



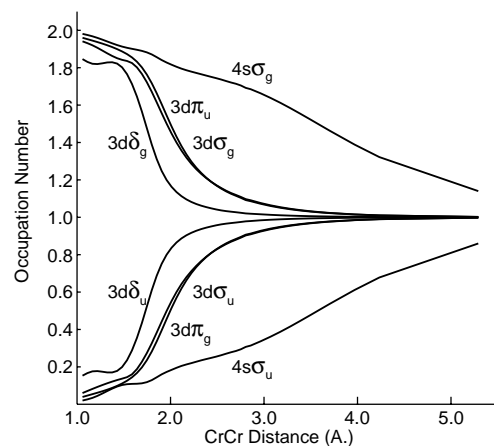
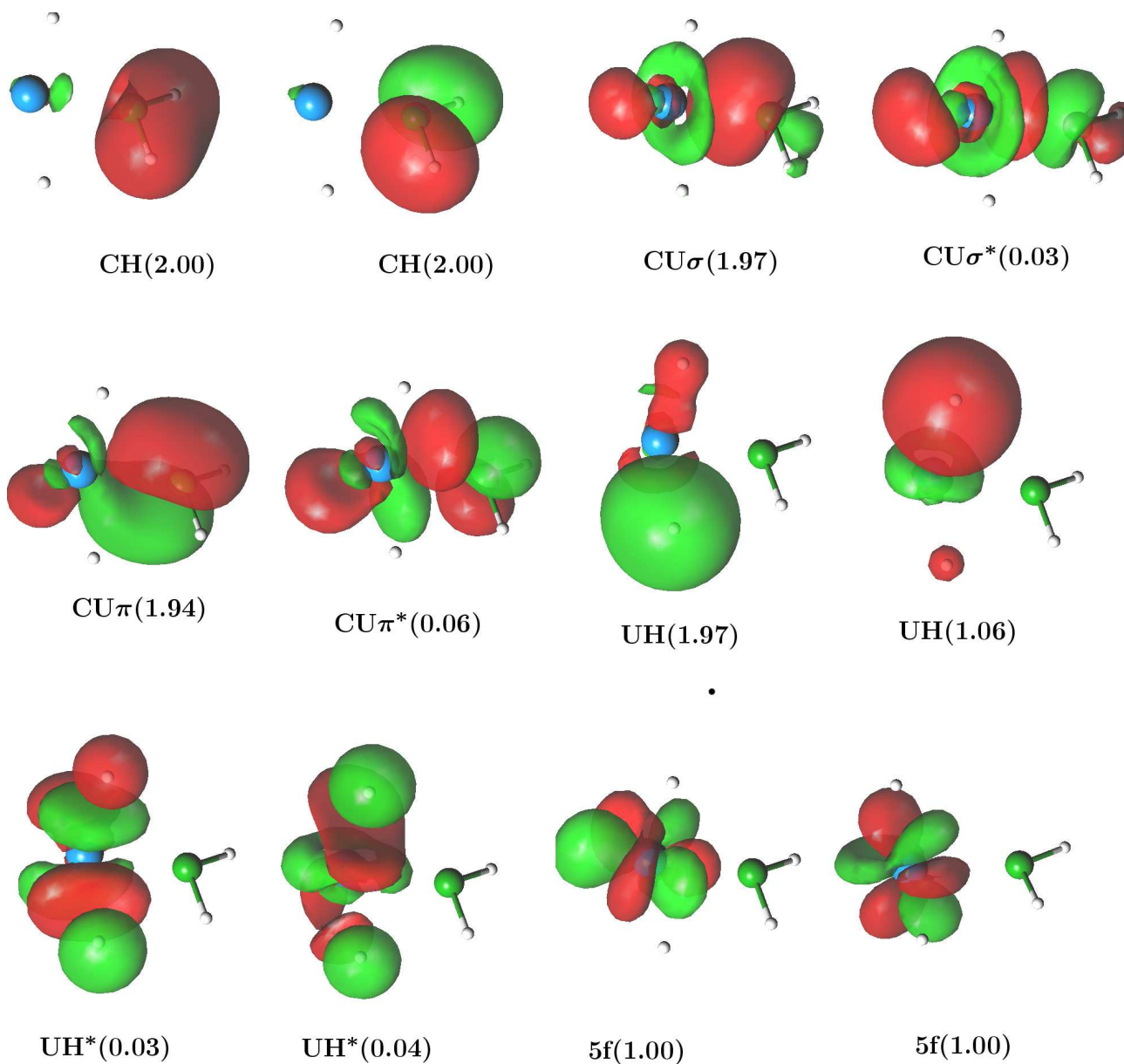
How to pick the active space (From B. O. Roos):

- Sometimes trivial, sometimes more difficult, sometimes impossible. It is necessary to know something about the electronic structure!
- Two problems must be solved: The number of active orbitals in each symmetry **and the shape of them (the input orbitals)**
- Use MOLCAS-GV to identify the orbitals in the active space.
- In difficult cases, run RASSCF calculations with larger active space Ideally: orbitals with occupation numbers in the range 0.02-1.98 should be active.

Examples: Cr_2 , H_2CUH_2

The Cr_2 molecule has 12 electrons in 12 active orbitals.

In the H_2CUH_2 molecule, the active CH orbitals can be excluded, if the CH bonds are kept fixed. This calculation used 13 electrons in 12 active orbitals.



How to pick the active space (From B. O. Roos):

Main group atoms: Of course a full valence CASSCF is usually the best choice, but not possible except for very small molecules. For N, O, and F the 2s is not needed. CH bonds can often be left inactive. Long alkyl chains with an active group at the end only needs active orbitals there. The choice of active space does not automatically limit the size of molecules that can be studied.

Excited states of planar unsaturated molecules: All π -orbitals should be active, if possible. Otherwise, select on energy criteria, and on how many/which states that should be computed. For higher energies (> 5 eV for first row), include a special Rydberg basis set. Place it at computed center of charge of the cation. Consult e.g. the Valencia group.

Transition metal compounds: This is a more difficult case. **Recommended reading:** K. Pierloot, *Mol. Phys.* 101, 2083 (2003). Generally, all orbitals that have d-character should be included. For example: $\text{Cr}(\text{CO})_6$, $\text{Fe}(\text{CO})_5$ and $\text{Ni}(\text{CO})_4$ need 10 active electrons in 10 orbitals. For Cr-Cu one needs to account for the **double shell effect**, at least if the d-orbital occupation changes in the process studied.

How to pick the active space (From B. O. Roos):

Transition metal compounds, cont:d: High oxidation numbers gives more covalent bonds (charge transfer) and need more active orbitals: Ex.: MnO_4^- : 24 in 17 (all 3d and O(2p))

Lanthanides: The 4f shell is inert but has to be kept active.

5d,6s (6p) the most important orbitals.

Often very ionic complexes: Only 4f active.

Covalent bonds difficult because large demands on the active space. High spin in the f-shell helps (ex: Gd_2 , $S=7$).

Actinides: In principle: 5f,6d,7s active (13 orbitals).

But: actinides are often highly charged: only 5f active.

But: covalent bonding is not unusual. Example uranyl, UO_2^{2+} , which needs a 12 in 12 active space.

Beware: nothing is trivial in actinide chemistry.

Intensities and RASSI

Intensities are obtained from matrix elements of (typically) the dipole operator over the states of interest. This is one of the main usages for the RASSI program, which can compute matrix elements of any one-electron operator over a set of RASSCF wave functions, as long as the required integrals have been computed by the Seward program.

The procedure can be summarized:

- For each pair of wave functions, transform their orbitals to a biorthonormal system. Transform the corresponding CI wave functions to the new basis.
- It is now easy to compute transition density matrices (1- and 2-). Routinely used to compute matrix elements.
- If the RASSCF states were not orthogonal and non-interacting, compute the Hamiltonian matrix elements. Solve the SI (State Interaction) problem.
- Can be used with many RAS states (more than 200 have been used).

What is wrong with non-relativistic quantum chemistry?

Relativistic corrections will systematically affect the chemistry of the heavier elements:

- Atomic ionization potentials, electron affinities, and excitation energies affect the energies of dissociation asymptotes, and thus the potential curves for bond breaking and positions and height of barriers.
- Open shells of radicals, transition metal compounds, lanthanide and actinide compounds, and excited states undergo spin-orbit splitting.
- There are often a multitude of low-lying electronic states for some or all conformations, especially along bond-breaking parts of reaction paths. Intrasystem interactions make them all relevant to reactivity.

The CASSCF/CASPT2/SO-RASSI approach

For heavy elements, relativistic effects including SO coupling affects structure and even chemical valence.

In recent years, we have worked out a combination of quantum chemical methods that seems able to handle many systems involving such elements, at a satisfactory level of accuracy. Radicals, exotic bond types and excited states are all handled at a uniform level of approximations.

This approach has by now been applied to a number of chemical and spectroscopic problems: see e.g. a recent article in PCCP 6, 2919 (2004).

The Dirac Hamiltonian (in an external static em field)

The conventional relativistic dynamics for an electron in a static four-potential, $A_\mu = (\phi/c, -\mathbf{A})$, is determined by the Lagrangian

$$\mathcal{L} = -m_e c^2 \sqrt{1 - u^2/c^2} - e\mathbf{A} \cdot \mathbf{u} + e\phi$$

where \mathbf{u} is the velocity. (Note: The electron charge is $-e$.)

The canonical momentum is thus

$$\mathbf{p} = \frac{\partial \mathcal{L}}{\partial \mathbf{u}} = \frac{m_e \mathbf{u}}{\sqrt{1 - u^2/c^2}} - e\mathbf{A}$$

and the Hamiltonian is obtained when $\mathbf{p}\mathbf{u} - \mathcal{L}$ is reexpressed as a function of \mathbf{p} :

$$\mathcal{H} = c\sqrt{m_e^2 c^2 + (\mathbf{p} + e\mathbf{A})^2} - e\phi$$

The Dirac Hamiltonian, continued

Dirac used a Clifford algebra generated by four quantities $(\beta, \boldsymbol{\alpha})$, where $\boldsymbol{\alpha} = (\alpha_x, \alpha_y, \alpha_z)$ are three anticommuting square roots of -1 , $\boldsymbol{\alpha}\beta = -\beta\boldsymbol{\alpha}$, and $\beta^2 = 1$. With this algebra,

$$\mathcal{H} = c\sqrt{m_e^2c^2 + (\mathbf{p} + e\mathbf{A})^2} - e\phi = c\boldsymbol{\alpha} \cdot (\mathbf{p} + e\mathbf{A}) + \beta m_e c^2 - e\phi$$

The canonical momentum \mathbf{p} is replaced by $-i\hbar\nabla$ in a representation where the state vectors are functions of position. Also, if we assume $\mathbf{A} = 0$ and replace $-e\phi$ with a potential energy V , we get the time-independent Dirac equation in the form used in quantum chemistry:

$$-i\hbar c\boldsymbol{\alpha} \cdot \nabla\Psi + (\beta m_e c^2 + V)\psi = E\Psi$$

The noncommutative quantities cannot be represented by structureless scalars, but can be represented by matrices. This requires wave functions to have several components. **At least four-dimensional matrices are needed.**

The Douglas-Kroll-Hess Hamiltonian

The Douglas-Kroll (DK) transformation is a sequence of unitary transformations that remove the coupling of the large and small components of the Dirac one-electron through some order in the one-electron external potential \hat{V} .

An ∞ -order DK transformation achieves an **exact** splitting of the Dirac Hamiltonian into two uncoupled two-component parts, one for the positive-energy and one for the negative-energy orbitals.

The lowest-order Hamiltonian is obtained by the transformation to a representation where energy, momentum and helicity are simultaneously diagonalized for the free fields. The kinetic energy is already relativistic. **The external potential, after transforming, yields the other relativistic corrections.**

The Douglas-Kroll-Hess transformation

The Dirac Hamiltonian is

$$\hat{H} = \hat{V} + E_0\hat{\beta} + c\hat{\mathbf{p}}\hat{\boldsymbol{\alpha}}$$

where \hat{V} is the external potential, $E_0 = m_e c^2$ is the rest mass energy of the electron, and the other symbols are the standard ones in relativistic quantum mechanics.

The free-field Hamiltonian is the same without the term \hat{V} . It is easily shown to be diagonalized by the unitary transformation matrix

$$\hat{U} = (2E_p(E_0 + E_p))^{-1/2} (E_0 + E_p + c\hat{\mathbf{p}}\hat{\boldsymbol{\alpha}}\hat{\beta})$$

in a basis of plane helicity waves.

The energy eigenvalues of these states are just the relativistic kinetic energy, $\pm E_p$, where

$$E_p = \sqrt{E_0^2 + p^2 c^2}$$

A one-electron basis set approach.

Hess suggested that a suitable basis set would allow a matrix representation of the operators \hat{A} and \hat{R} , which are algebraic functions of $\hat{\mathbf{p}}$:

$$\begin{aligned}\hat{U}_0 &= \hat{A} (1 + \hat{R}\hat{\beta}) \\ \hat{A} &= \sqrt{\frac{2E_p}{E_0 + E_p}} \\ \hat{R} &= \frac{c\hat{\mathbf{p}}\hat{\alpha}}{E_0 + E_p} \\ \Rightarrow \hat{U}_0^\dagger \hat{H}_0 \hat{U}_0 &= E_p \hat{\beta}\end{aligned}$$

and that this approach could easily be extended to higher orders. The resulting transformed potential terms can be subdivided into spin-free and spin-orbit terms.

In our approach, they are used separately.

We use a spin-free, or scalar, DK transformation when computing the conventional one-electron integrals. The two-electron integrals are used untransformed; this is known to be a workable approximation.

The Spin-Orbit Hamiltonian

The **one-electron term** of the no-pair spin-orbit Hamiltonian is

$$\hat{H}_{\text{SO}}^{\text{1el}} = \sum_k \left(\frac{A_k}{E_k + mc^2} \right) i\sigma_k \cdot \left((p_k V_{\text{ext}}(r_k) \times p_k) \left(\frac{A_k}{E_k + mc^2} \right) \right)$$

(adopted from a manuscript by B. Schimmelpfennig. Notation is conventional).

The **two-electron term** has **two contributions**:

$$\begin{aligned} \hat{H}_{\text{SO}}^{\text{2el}} &= \sum_{k \neq l} A_k A_l \left(\frac{i\sigma_k}{E_k + mc^2} \cdot \left(\left(p_k \frac{1}{r_{kl}} \right) \times p_k \right) \frac{1}{E_k + mc^2} \right) A_k A_l \\ &+ \sum_{k \neq l} A_k A_l \left(\frac{2i\sigma_k}{E_k + mc^2} \cdot \left(\left(p_l \frac{1}{r_{kl}} \right) \times p_l \right) \frac{1}{E_l + mc^2} \right) A_k A_l \end{aligned}$$

2nd quantized form of $\hat{H}_{\text{SO}}^{1\text{el}}$

Using spin-restricted orbitals, each term of the Hamiltonian is a scalar product of two vectors. One is a **vector-valued integral**, the other a **vector excitation operator**:

$$\hat{H}_{\text{SO}}^{1\text{el}} = \sum_{pq} \left(V_{pq}^x \hat{T}_{pq}^x + V_{pq}^y \hat{T}_{pq}^y + V_{pq}^z \hat{T}_{pq}^z \right)$$

where

$$\hat{T}_{pq}^x = \frac{1}{2} \left(\hat{p}_\alpha^\dagger \hat{q}_\beta + \hat{p}_\beta^\dagger \hat{q}_\alpha \right)$$

$$\hat{T}_{pq}^y = \frac{i}{2} \left(-\hat{p}_\alpha^\dagger \hat{q}_\beta + \hat{p}_\beta^\dagger \hat{q}_\alpha \right)$$

$$\hat{T}_{pq}^z = \frac{1}{2} \left(\hat{p}_\alpha^\dagger \hat{q}_\alpha - \hat{p}_\beta^\dagger \hat{q}_\beta \right)$$

2nd quantized form of $\hat{H}_{\text{SO}}^{2\text{el}}$

The corresponding two-electron terms are similar:

$$\hat{H}_{\text{SO}}^{2\text{el}} = \sum_{pqrs} \left(W_{pqrs}^x \hat{T}_{pqrs}^x + W_{pqrs}^y \hat{T}_{pqrs}^y + W_{pqrs}^z \hat{T}_{pqrs}^z \right)$$

if we simply define **two-electron vector excitation operators**,

$$\hat{T}_{pqrs}^x = \hat{T}_{pq}^x \hat{E}_{rs} - \delta_{rq} \hat{T}_{ps}^x$$

where the vector integrals can be simply expressed in the spin-other-orbit and spin-same-orbit integrals, which turn out to be identical apart from a simple index permutation.

But without going into any details, we note that the two-electron expression can be fairly well **approximated by a one-electron Hamiltonian**, e.g. as done by Marian, Wahlgren et al. This involves essentially the contraction of the two-electron vector integrals over a one-particle reference density matrix.

Spin-Orbit RASSI

For the purposes of computing spin-orbit matrix elements, we use RASSI to compute so-called **Wigner-Eckart-reduced density matrix elements** σ_{pq}^{AB} for each pair of states (A,B). These are **contracted with AMFI integrals** to form

$$V^{ABx} = \sum_{pq} \sigma_{pq}^{AB} V_{pq}^x$$

$$V^{ABy} = \sum_{pq} \sigma_{pq}^{AB} V_{pq}^y$$

$$V^{ABz} = \sum_{pq} \sigma_{pq}^{AB} V_{pq}^z$$

which are reduced matrix elements of the spin-orbit Hamiltonian, over the spin-free basis. We then apply the **Wigner-Eckart theorem** to produce the matrix elements over all the spin components.

The SO-coupling Hamiltonian matrix elements

In a Hamiltonian matrix **over individual spin states**, the following contributions can then be calculated and added to the spin-free Hamiltonian matrix, as follows:

$$\langle SM | \hat{H}^{\text{SO}} | S+1 M \pm 1 \rangle = -\frac{\sqrt{(S \pm M + 1)(S \pm M + 2)}}{2} (\pm V^{ABx} + iV^{ABy}) \quad (1)$$

$$\langle SM | \hat{H}^{\text{SO}} | S+1 M \rangle = \sqrt{(S+1)^2 - M^2} V^{ABz} \quad (2)$$

$$\langle SM | \hat{H}^{\text{SO}} | S M \pm 1 \rangle = \pm \frac{\sqrt{(S \mp M)(S \pm M + 1)}}{2} (\pm V^{ABx} + iV^{ABy}) \quad (3)$$

$$\langle SM | \hat{H}^{\text{SO}} | S M \rangle = MV^{ABz} \quad (4)$$

$$\langle SM | \hat{H}^{\text{SO}} | S-1 M \pm 1 \rangle = \frac{\sqrt{(S \mp M)(S \mp M - 1)}}{2} (\pm V^{ABx} + iV^{ABy}) \quad (5)$$

$$\langle SM | \hat{H}^{\text{SO}} | S-1 M \rangle = \sqrt{S^2 - M^2} V^{ABz} \quad (6)$$

SO-RASSI Example, I₂

