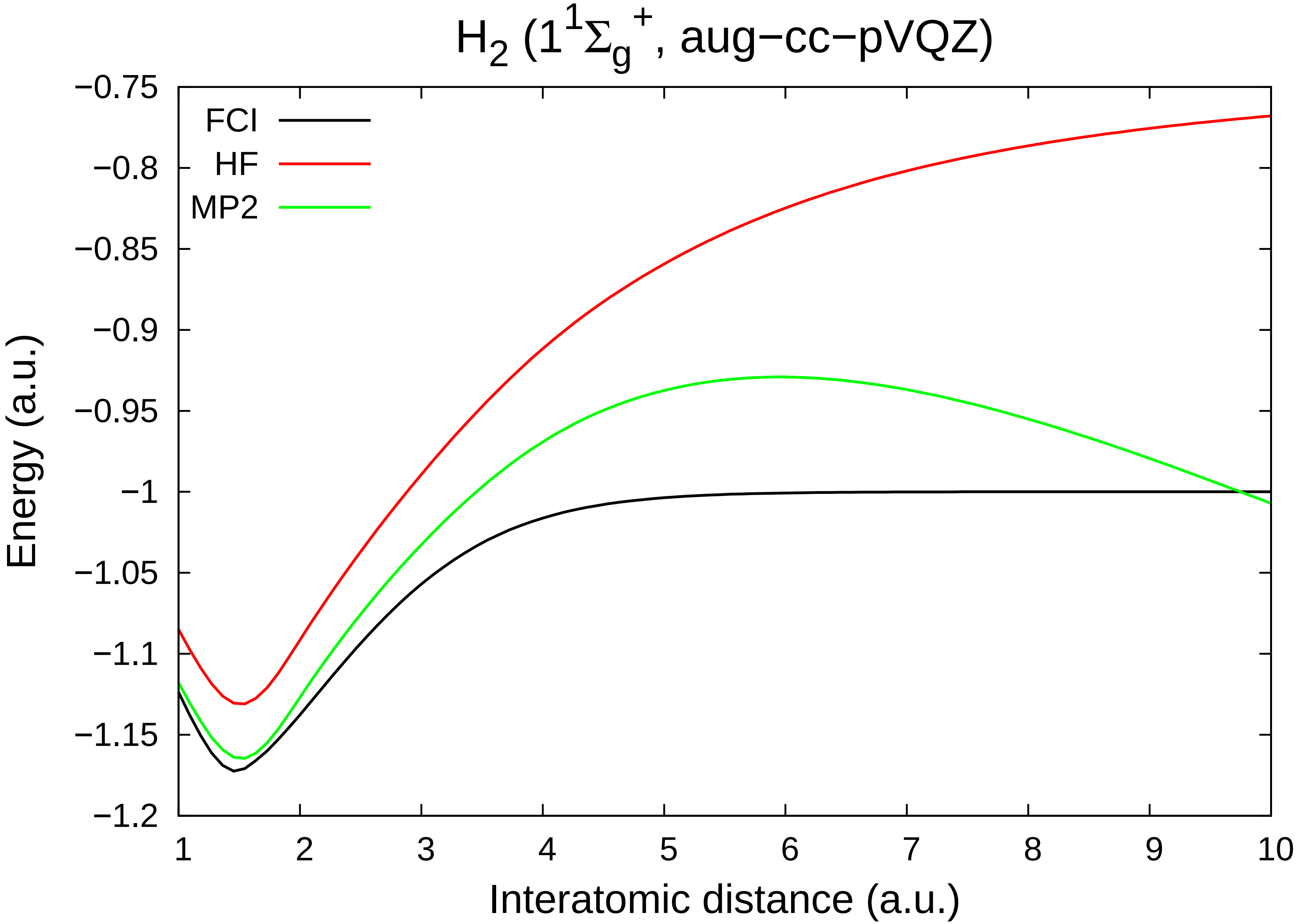
Introduction to multiconfigurational quantum chemistry

Emmanuel Fromager

Institut de Chimie de Strasbourg - Laboratoire de Chimie Quantique -
Université de Strasbourg /CNRS

Second school in computational physics, Les Houches, France, 28.06.12


H_2 ($1^1\Sigma_g^+$, aug−cc−pVQZ)
FCI
HF
MP2
Energy (a.u.)
−0.75
−0.8
−0.85
−0.9
−0.95
−1
−1.05
−1.1
−1.15
−1.2
1
2
3
4
5
6
7
8
9
10
Interatomic distance (a.u.)

Static correlation

- H_2 in the equilibrium geometry:

$$\boxed{|\Psi_0\rangle = C_0|1\sigma_g^\alpha 1\sigma_g^\beta\rangle + \ldots} \quad \text{where } |C_0|^2 = 98\%$$

no static correlation

- In the dissociation limit: $H_A \ldots H_B$ and NOT $H_A^- \ldots H_B^+$ or $H_A^+ \ldots H_B^-$

$$\phi_{1\sigma_g}(\mathbf{r}) = \frac{1}{\sqrt{2}}\Big(\phi_{1s_A}(\mathbf{r}) + \phi_{1s_B}(\mathbf{r})\Big) \quad \text{and} \quad \phi_{1\sigma_u}(\mathbf{r}) = \frac{1}{\sqrt{2}}\Big(\phi_{1s_A}(\mathbf{r}) - \phi_{1s_B}(\mathbf{r})\Big)$$

$$|1\sigma_g^\alpha 1\sigma_g^\beta\rangle = \frac{1}{2}\Big(|1s_A^\alpha 1s_B^\beta\rangle + |1s_B^\alpha 1s_A^\beta\rangle + |1s_A^\alpha 1s_A^\beta\rangle + |1s_B^\alpha 1s_B^\beta\rangle\Big)$$

$$-|1\sigma_u^\alpha 1\sigma_u^\beta\rangle = \frac{1}{2}\Big(|1s_A^\alpha 1s_B^\beta\rangle + |1s_B^\alpha 1s_A^\beta\rangle - |1s_A^\alpha 1s_A^\beta\rangle - |1s_B^\alpha 1s_B^\beta\rangle\Big)$$

$$\boxed{|\Psi_0\rangle = \frac{1}{\sqrt{2}}\Big(|1\sigma_g^\alpha 1\sigma_g^\beta\rangle - |1\sigma_u^\alpha 1\sigma_u^\beta\rangle\Big)}$$

strong static correlation

- Exact ground-state wave function in the dissociation limit:

$$\Psi_0(\mathbf{r_1},\sigma_1,\mathbf{r_2},\sigma_2) = \Psi_0(\mathbf{r_1},\mathbf{r_2})\frac{1}{\sqrt{2}}\Big(\alpha(\sigma_1)\beta(\sigma_2) - \alpha(\sigma_2)\beta(\sigma_1)\Big)$$

where $\Psi_0(\mathbf{r_1},\mathbf{r_2}) = \phi_{1\sigma_g}(\mathbf{r_1})\phi_{1\sigma_g}(\mathbf{r_2}) - \phi_{1\sigma_u}(\mathbf{r_1})\phi_{1\sigma_u}(\mathbf{r_2})$

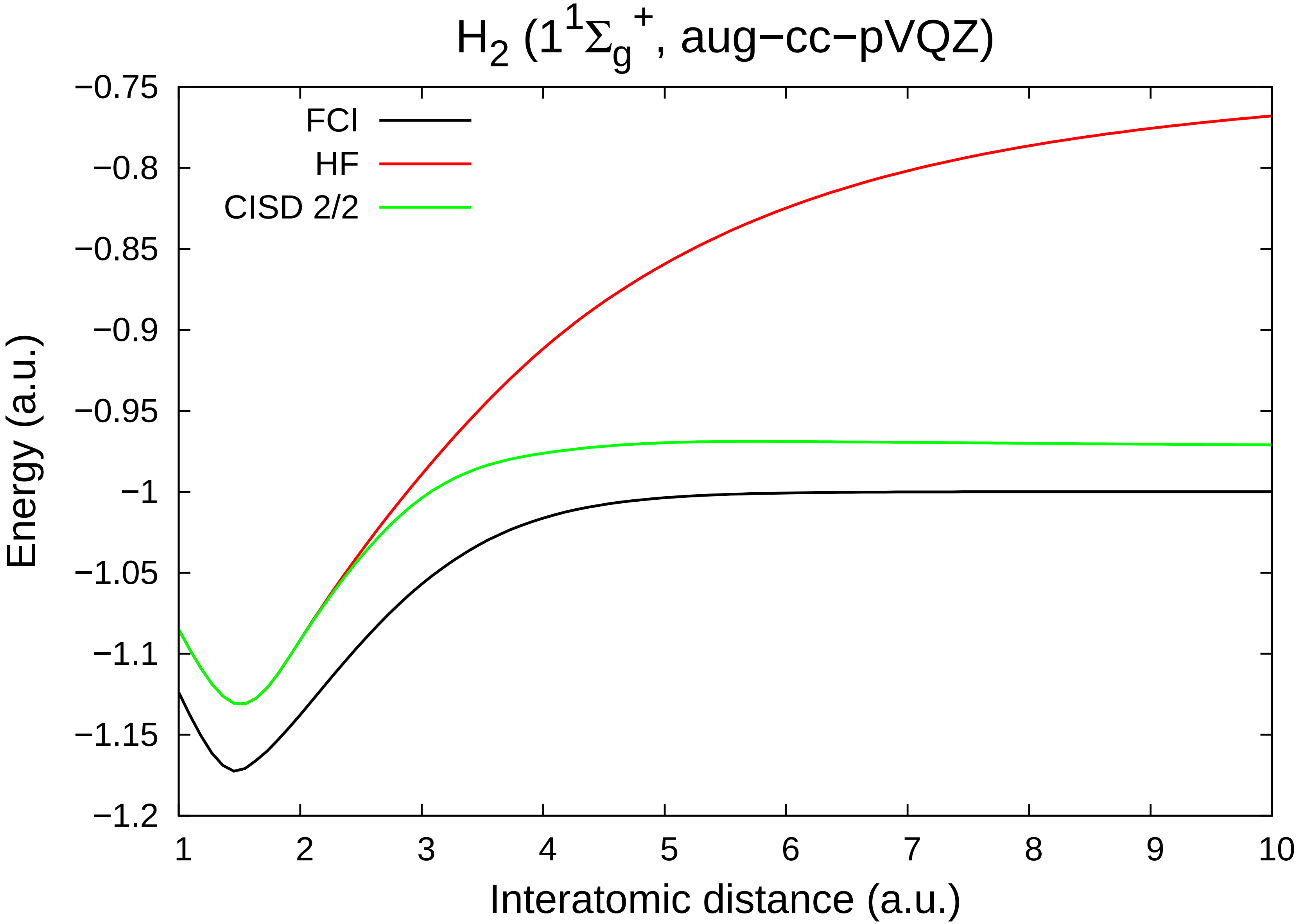
- If electron 1 is bound to H$_A$, around $\mathbf{r_2} = \mathbf{r_1}$ we have $\boxed{|\mathbf{r_1}-\mathbf{r_2}| << |\mathbf{r_1}-\mathbf{r_A}| << |\mathbf{r_B}-\mathbf{r_A}|}$

$$\phi_{1s_B}(\mathbf{r_2}) = \phi_{1s}(|\mathbf{r_2}-\mathbf{r_B}|) = \phi_{1s}(|\mathbf{r_2}-\mathbf{r_1}+\mathbf{r_1}-\mathbf{r_A}+\mathbf{r_A}-\mathbf{r_B}|) \approx \phi_{1s}(|\mathbf{r_A}-\mathbf{r_B}|)$$
$$\phi_{1s_B}(\mathbf{r_1}) = \phi_{1s}(|\mathbf{r_1}-\mathbf{r_B}|) = \phi_{1s}(|\mathbf{r_1}-\mathbf{r_A}+\mathbf{r_A}-\mathbf{r_B}|) \approx \phi_{1s}(|\mathbf{r_A}-\mathbf{r_B}|)$$

$$\Psi_0(\mathbf{r_1},\mathbf{r_2}) \approx \phi_{1s}(|\mathbf{r_A}-\mathbf{r_B}|)\Big(\phi_{1s}(|\mathbf{r_1}-\mathbf{r_A}|) + \phi_{1s}(|\mathbf{r_2}-\mathbf{r_A}|)\Big)$$

$$\phi_{1s}(r) = e^{-\zeta r} \quad \longrightarrow \quad \boxed{\Psi_0(\mathbf{r_1},\mathbf{r_2}) \approx e^{-\zeta|\mathbf{r_A}-\mathbf{r_B}|}}$$

Conclusion: static correlation has nothing to do with the cusp condition ... It is here a long-range type of correlation (left/right correlation)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FCI
HF
CISD 2/2

Multi-Configurational Self-Consistent Field model (MCSCF)

- The MCSCF model consists in performing a CI calculation with a reoptimization of the orbitals

$$|\Psi(\boldsymbol{\kappa},\mathbf{C})\rangle = e^{-\hat{\kappa}}\left(\sum_i C_i|i\rangle\right)$$

- The MCSCF model is a multiconfigurational extension of HF which aims at describing static correlation: a limited number of determinants should be sufficient.
- Short-range dynamical correlation is treated afterwards (post-MCSCF models)
- Choice of the determinants: active space

H. . .H	2 electrons in 2 orbitals $(1\sigma_g, 1\sigma_u)$	$\longrightarrow$	2/2
Be	2 electrons in 4 orbitals $(2s, 2p_x, 2p_y, 2p_z)$	$\longrightarrow$	2/4

Multi-Configurational Self-Consistent Field model (MCSCF)

- Complete Active Space (CAS) for Be: $|1s^2 2s^2\rangle, |1s^2 2p_x^2\rangle, |1s^2 2p_y^2\rangle, |1s^2 2p_z^2\rangle,$

  if all the determinants are included in the MCSCF calculation $\longrightarrow$ CASSCF

  if a Restricted Active Space (RAS) is used $\longrightarrow$ RASSCF

- The orbital space is now divided in three:

doubly occupied molecular orbitals (inactive)	$\phi_i, \phi_j, \ldots$	$1s$
active molecular orbitals	$\phi_u, \phi_v, \ldots$	$2s, 2p_x, 2p_y, 2p_z$
unoccupied molecular orbitals	$\phi_a, \phi_b, \ldots$	$3s, 3p, 3d, \ldots$

Multi-Configurational Self-Consistent Field model (MCSCF)

EX6: In order to illustrate with H_2 the fact that active orbitals can be partially occupied, show that the active part of the density matrix ${}^{A}\mathbf{D}$, defined as

$$ {}^{A}\mathbf{D}_{vw} = \langle \Psi | \hat{E}_{vw} | \Psi \rangle, $$

where $|\Psi\rangle = \dfrac{1}{\sqrt{1+c^2}} \Big(|1\sigma_g^\alpha 1\sigma_g^\beta\rangle - c|1\sigma_u^\alpha 1\sigma_u^\beta\rangle \Big)$,

equals

$$ {}^{A}\mathbf{D} = \begin{bmatrix} \dfrac{2}{1+c^2} & 0 \\ 0 & \dfrac{2c^2}{1+c^2} \end{bmatrix}. $$

Note: In the particular case of a single determinantal wave function ($c = 0$) the active density matrix reduces to $\begin{bmatrix} 2 & 0 \\ 0 & 0 \end{bmatrix}$.

- Iterative optimization of the orbital rotation vector $\boldsymbol{\kappa}$ and the CI coefficients C_i:

$$|\Psi^{(0)}\rangle = \sum_i C_i^{(0)}|i\rangle \quad \longleftarrow \quad \text{normalized starting wave function}$$

$$|\Psi(\boldsymbol{\lambda})\rangle = e^{-\hat{\kappa}}\,\frac{|\Psi^{(0)}\rangle + \hat{Q}|\boldsymbol{\delta}\rangle}{\sqrt{1+\langle\boldsymbol{\delta}|\hat{Q}|\boldsymbol{\delta}\rangle}} \quad \longleftarrow \quad \text{convenient parametrization} \quad \boldsymbol{\lambda} = \begin{bmatrix} \vdots \\ \kappa_{pq} \\ \vdots \\ \delta_i \\ \vdots \end{bmatrix} \quad p > q$$

$$\hat{Q} = 1 - |\Psi^{(0)}\rangle\langle\Psi^{(0)}|, \qquad |\boldsymbol{\delta}\rangle = \sum_i \delta_i |i\rangle, \qquad \langle\Psi^{(0)}|\hat{Q}|\boldsymbol{\delta}\rangle = 0, \qquad \langle\Psi(\boldsymbol{\lambda})|\Psi(\boldsymbol{\lambda})\rangle = 1$$

- MCSCF energy expression: $E(\boldsymbol{\lambda}) = \langle\Psi(\boldsymbol{\lambda})|\hat{H}|\Psi(\boldsymbol{\lambda})\rangle$

- Variational optimization: $\boxed{E^{[1]}_{\boldsymbol{\lambda}_+} = \begin{bmatrix} E^{\mathrm{o}[1]}_{\boldsymbol{\lambda}_+} \\ E^{\mathrm{c}[1]}_{\boldsymbol{\lambda}_+} \end{bmatrix} = 0}$ where $E^{\mathrm{o}[1]}_{\boldsymbol{\lambda}_+} = \left.\dfrac{\partial E(\boldsymbol{\lambda})}{\partial \boldsymbol{\kappa}}\right|_{\boldsymbol{\lambda}_+}$

and $E^{\mathrm{c}[1]}_{\boldsymbol{\lambda}_+} = \left.\dfrac{\partial E(\boldsymbol{\lambda})}{\partial \boldsymbol{\delta}}\right|_{\boldsymbol{\lambda}_+}$

- Newton method:

$$E(\boldsymbol{\lambda}) \approx E(0) + \boldsymbol{\lambda}^T E_0^{[1]} + \frac{1}{2}\boldsymbol{\lambda}^T E_0^{[2]}\boldsymbol{\lambda} \quad \rightarrow \quad E_{\boldsymbol{\lambda}_+}^{[1]} \approx E_0^{[1]} + E_0^{[2]}\boldsymbol{\lambda}_+ = 0 \quad \rightarrow \quad E_0^{[2]} \underbrace{\boldsymbol{\lambda}_+}_{\textbf{Newton step}} = -E_0^{[1]}$$

- Convergence reached when $E_0^{[1]} = 0$

EX7: Show that $E_{0,pq}^{\mathrm{o}[1]} = \langle \Psi^{(0)} | [\hat{E}_{pq} - \hat{E}_{qp}, \hat{H}] | \Psi^{(0)} \rangle$ and $E_0^{c[1]} = 2\Big(\mathbf{H}^{\mathrm{CAS}} - E(0)\Big)\mathbf{C}^{(0)}$

where $\mathbf{H}_{ij}^{\mathrm{CAS}} = \langle i | \hat{H} | j \rangle$ and $\mathbf{C}^{(0)} = \begin{bmatrix} \vdots \\ C_i^{(0)} \\ \vdots \end{bmatrix}$

Note: $E_0^{\mathrm{o}[1]} = 0$ is known as generalized Brillouin theorem.

Multi-Configurational Self-Consistent Field model (MCSCF)

EX8: We consider in this exercise a different parametrization of the MCSCF wave function:

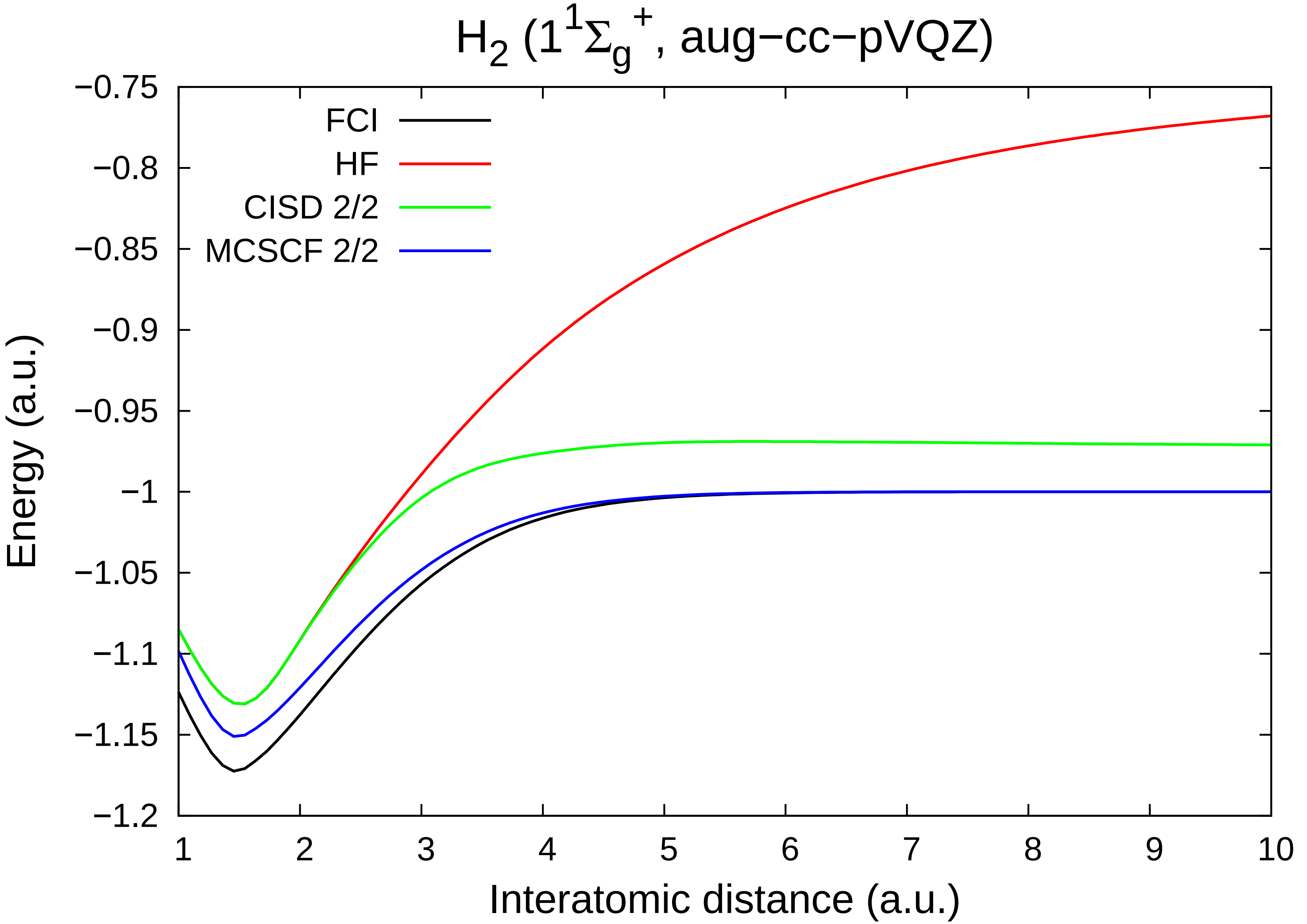
$$|\Psi(\boldsymbol{\kappa},\mathbf{S})\rangle = e^{-\hat{\kappa}}\, e^{-\hat{S}}|\Psi^{(0)}\rangle$$

where $\hat{S} = \sum_K S_K \Big(|K\rangle\langle\Psi^{(0)}| - |\Psi^{(0)}\rangle\langle K|\Big)$, $\quad \langle\Psi^{(0)}|K\rangle = 0, \quad \langle K|K'\rangle = \delta_{KK'}$ and

$$\sum_i |i\rangle\langle i| = |\Psi^{(0)}\rangle\langle\Psi^{(0)}| + \sum_K |K\rangle\langle K|$$

Derive the corresponding MCSCF gradient and show that the optimized MCSCF wave functions obtained with this parametrization and the previous one are the same.

Note: This double exponential form is convenient for computing response properties at the MCSCF level and performing state-averaged MCSCF calculations.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Multi-Reference Perturbation Theory (MRPT)

- Multiconfigurational extension of MP2:

unperturbed wave function $|\Phi_0\rangle \longrightarrow |\Psi^{(0)}\rangle$

unperturbed energy $E^{(0)} = 2\sum_i \varepsilon_i \longrightarrow ???$

perturbers $|D\rangle \longrightarrow ???$

zeroth-order excited energies $E^{(0)} + \varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j \longrightarrow ???$

unperturbed Hamiltonian $\hat{F} \longrightarrow E^{(0)}|\Phi_0\rangle\langle\Phi_0| + \sum_D \langle D|\hat{F}|D\rangle|D\rangle\langle D| \longrightarrow ???$

Multi-Reference Perturbation Theory (MRPT)

- MCSCF Fock operator: $\hat{F} = \sum_{p,q} f_{pq} \hat{E}_{pq}$

$$f_{pq} = h_{pq} + \sum_{rs} \Big(\langle pr|qs\rangle - \frac{1}{2} \langle pr|sq\rangle \Big) D_{rs} \quad \text{and} \quad D_{rs} = \langle \Psi^{(0)} | \hat{E}_{rs} | \Psi^{(0)} \rangle$$

- The density matrix is split into inactive and active parts: $\mathbf{D} \;=\; {}^{I}\mathbf{D} + {}^{A}\mathbf{D}$

$${}^{I}D_{ij} = 2\delta_{ij}, \quad {}^{A}D_{uv} = \langle \Psi^{(0)} | \hat{E}_{uv} | \Psi^{(0)} \rangle$$

- In general, the MCSCF wave function $\Psi^{(0)}$ is not eigenfunction of the MCSCF Fock operator (which is a one-electron operator):

$\hat{H}^{\mathrm{CAS}} | \Psi^{(0)} \rangle = E_0 | \Psi^{(0)} \rangle,$ $\qquad E_0$: converged MCSCF energy

$\hat{H}^{\mathrm{CAS}} = \hat{P}^{\mathrm{CAS}} \; \hat{H} \; \hat{P}^{\mathrm{CAS}},$ $\qquad \hat{P}^{\mathrm{CAS}} = \sum_{i} |i\rangle\langle i|$

Multi-Reference Perturbation Theory (MRPT)

EX9: Show that the Hamiltonian and the Fock operator reduce, within the CAS space, to

$$\hat{H}^{\text{CAS}} = \left(2\sum_i h_{ii} + \sum_{i,j}\Big(2\langle ij|ij\rangle - \langle ij|ji\rangle\Big)\right)\hat{P}^{\text{CAS}}$$

$$+\sum_{uv}\left(h_{uv} + \sum_i \Big(2\langle ui|vi\rangle - \langle ui|iv\rangle\Big)\right)\hat{E}_{uv}\hat{P}^{\text{CAS}} + \frac{1}{2}\sum_{uvwx}\langle uw|vx\rangle\Big(\hat{E}_{uv}\hat{E}_{wx} - \delta_{vw}\hat{E}_{ux}\Big)\hat{P}^{\text{CAS}}$$

$$\hat{F}^{\text{CAS}} = \left(2\sum_i h_{ii} + 2\sum_{i,j}\Big(2\langle ij|ij\rangle - \langle ij|ji\rangle\Big)\right)\hat{P}^{\text{CAS}}$$

$$+\sum_{uv}\left(h_{uv} + \sum_i \Big(2\langle ui|vi\rangle - \langle ui|iv\rangle\Big)\right)\hat{E}_{uv}\hat{P}^{\text{CAS}} + \sum_{iuv}\Big(2\langle ui|vi\rangle - \langle ui|iv\rangle\Big)\,{}^{A}D_{uv}\hat{P}^{\text{CAS}}$$

$$+\sum_{uvwx}\Big(\langle uw|vx\rangle - \frac{1}{2}\langle uw|xv\rangle\Big)\,{}^{A}D_{wx}\hat{E}_{uv}\hat{P}^{\text{CAS}}$$

Multi-Reference Perturbation Theory (MRPT)

- MRPT2 based on $\hat{F}$ is known as CASPT2:

$$\hat{H}_0 = \underbrace{\langle\Psi^{(0)}|\hat{F}|\Psi^{(0)}\rangle}_{E^{(0)}} |\Psi^{(0)}\rangle\langle\Psi^{(0)}| + \hat{Q}\hat{H}_0\hat{Q}$$

At the CASPT2 level the zeroth-order energy does not equal the MCSCF one (as for MP2)

- MRPT2 based on $\hat{H}^{\mathrm{CAS}}$ is known as N-Electron Valence PT2 (NEVPT2):

$$\hat{H}_0 = \underbrace{\langle\Psi^{(0)}|\hat{H}^{\mathrm{CAS}}|\Psi^{(0)}\rangle}_{E_0} |\Psi^{(0)}\rangle\langle\Psi^{(0)}| + \hat{Q}\hat{H}_0\hat{Q}$$

At the NEVPT2 level the zeroth-order energy equals the MCSCF one.

Multi-Reference Perturbation Theory (MRPT)

- Choice of the perturbers: eight types of excitation subspaces for the first-order correction to the wave function

$S^{(0)}_{ij,ab} \;\; (j \geq i,\; b \geq a)$ $\quad$ $S^{(-1)}_{i,ab} \;\; (b \geq a)$ $\quad$ $S^{(+1)}_{ij,a} \;\; (j \geq i)$ $\quad$ $S^{(-2)}_{ab} \;\; (b \geq a)$

$S^{(+2)}_{ij} \;\; (j \geq i)$ $\quad$ $S^{(0)}_{i,a}$ $\quad$ $S^{(-1)}_{a}$ $\quad$ $S^{(+1)}_{i}$

- Contracted perturbation theory: for example, states in $S^{(-2)}_{ab}$ are expressed as

$$\hat{E}_{au}\hat{E}_{bv}|\Psi^{(0)}\rangle = \sum_i \underset{\displaystyle \downarrow}{C_i^{(0)}} \hat{E}_{au}\hat{E}_{bv}|i\rangle$$

optimized at the MCSCF level (kept frozen in the MRPT2 calculation)

- Unperturbed Hamiltonian in CASPT2:

$$\hat{H}_0 = \langle\Psi^{(0)}|\hat{F}|\Psi^{(0)}\rangle|\Psi^{(0)}\rangle\langle\Psi^{(0)}| + \Big(\hat{P}^{\mathrm{CAS}} - |\Psi^{(0)}\rangle\langle\Psi^{(0)}|\Big)\hat{F}\Big(\hat{P}^{\mathrm{CAS}} - |\Psi^{(0)}\rangle\langle\Psi^{(0)}|\Big)$$
$$+\Big(\sum_{k,l}\hat{P}_{S_l^{(k)}}\Big)\hat{F}\Big(\sum_{k,l}\hat{P}_{S_l^{(k)}}\Big)$$

  where $\hat{P}_{S_l^{(k)}}$ projects onto the excitation subspace $S_l^{(k)}$.

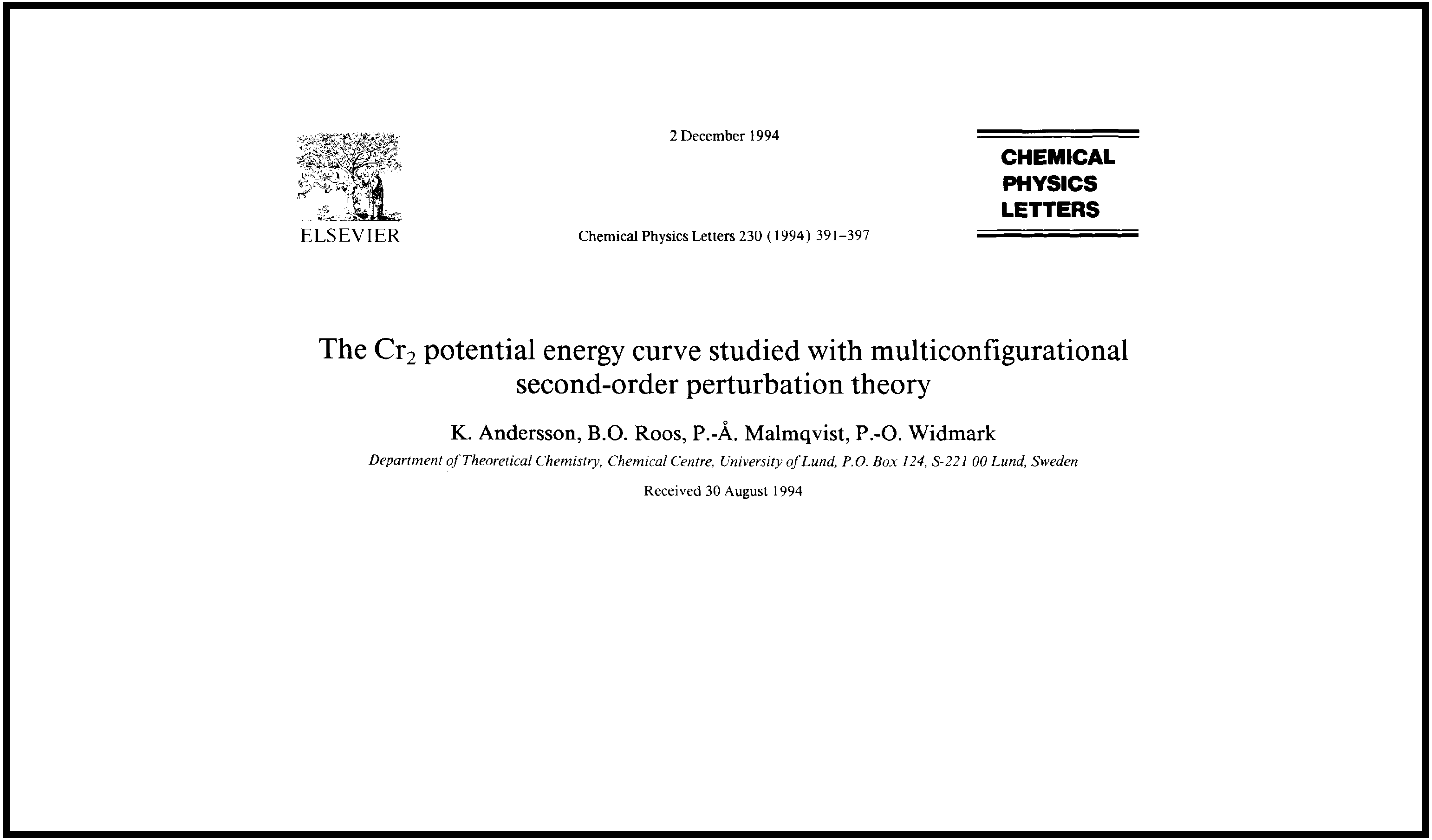
- Intruder state problem: $|\Psi^{(1)}\rangle = \sum_P \frac{|\Psi_P^{(0)}\rangle\langle\Psi_P^{(0)}|\hat{H}|\Psi^{(0)}\rangle}{E^{(0)} - E_P^{(0)}}$

  where $\langle\Psi_P^{(0)}|\hat{H}|\Psi^{(0)}\rangle$ is small and $E^{(0)} \approx E_P^{(0)}$

- Introduction of a level shift parameter ε:

$$E^{(0)} - E_P^{(0)} \quad\longrightarrow\quad E^{(0)} - E_P^{(0)} + \varepsilon$$

- Intruder state problems can be avoided when using a different zeroth-order Hamiltonian



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2 December 1994

Chemical Physics Letters 230 (1994) 391–397

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The Cr_2 potential energy curve studied with multiconfigurational second-order perturbation theory

K. Andersson, B.O. Roos, P.-Å. Malmqvist, P.-O. Widmark

Department of Theoretical Chemistry, Chemical Centre, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden

Received 30 August 1994

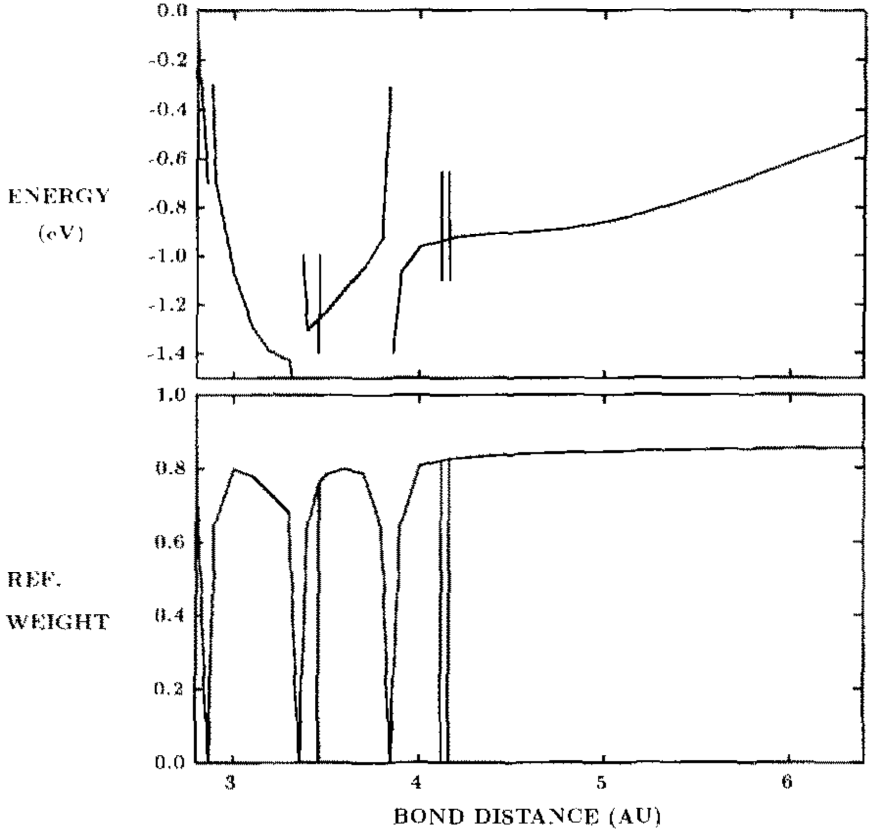
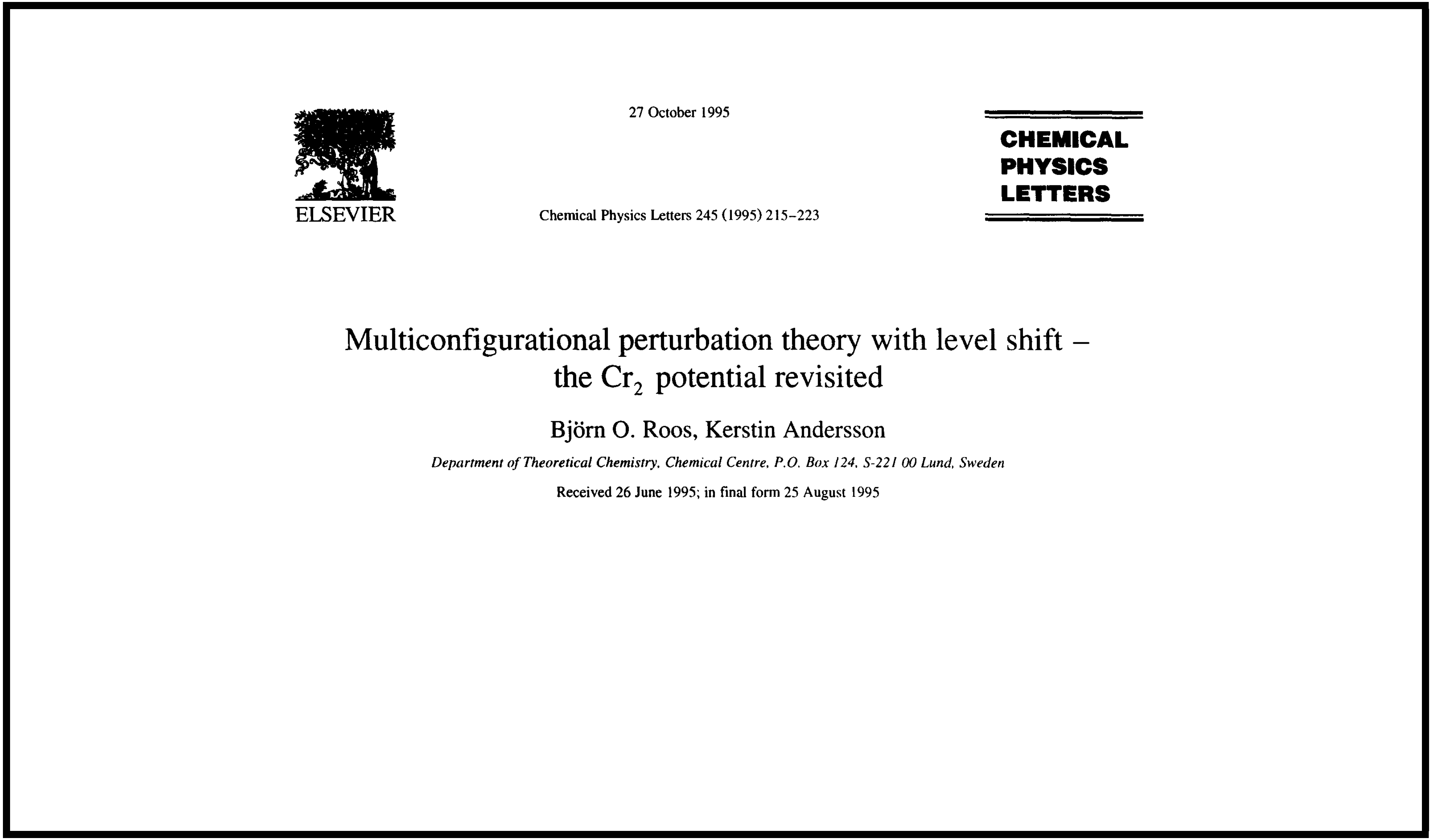


Fig. 4. The potential curve of Cr_2 obtained with CASPT2 above and the weight of the CASSCF wavefunction in the first-order wavefunction below. The basis set is of ANO type of size 8s7p6d4f and the active space is formed by 3d and 4s orbitals. The 3s, 3p correlation effects have been taken into account but no relativistic effects are included.



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27 October 1995

Chemical Physics Letters 245 (1995) 215–223

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Multiconfigurational perturbation theory with level shift – the Cr_2 potential revisited

Björn O. Roos, Kerstin Andersson

Department of Theoretical Chemistry, Chemical Centre, P.O. Box 124, S-221 00 Lund, Sweden

Received 26 June 1995; in final form 25 August 1995

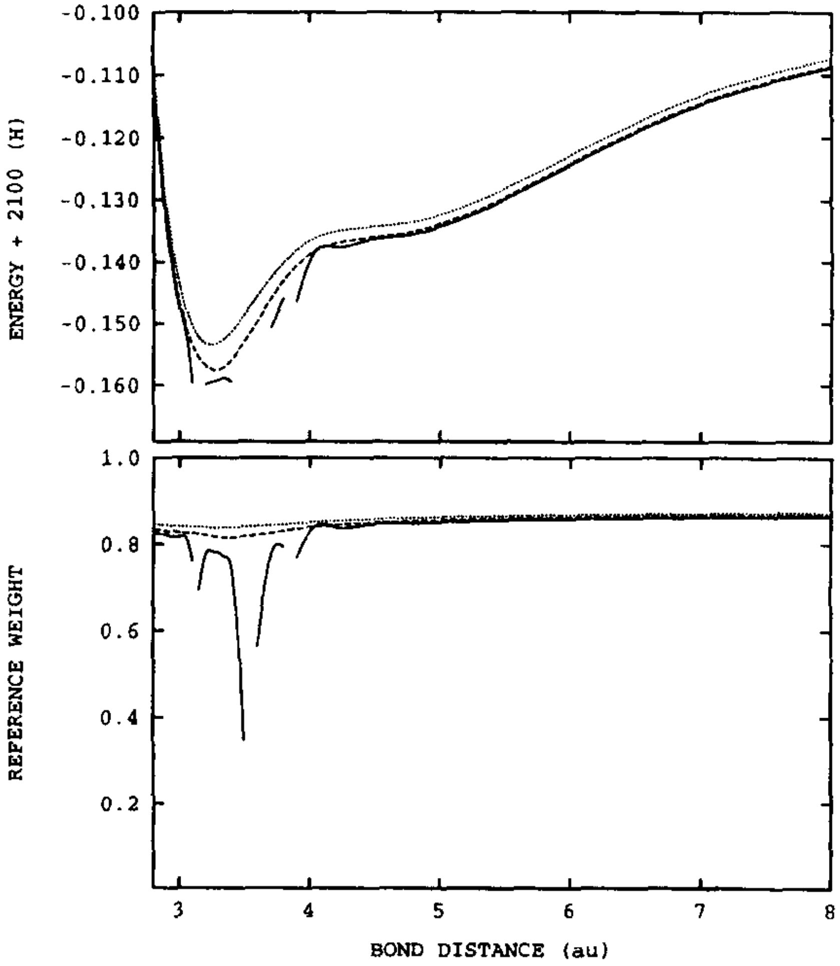


Fig. 2. The potential curve for the ground state of Cr_2 for three values of the level shift, 0.05 (solid line), 0.10, (dashed line), and 0.20 H (dotted line). The LS correction has been applied. The lower diagram gives the corresponding weight of the CASSCF reference function.

- Defining a two-electron Fock operator: Dyall's Hamiltonian

$$\varepsilon_i = -\langle \hat{a}_{i,\sigma}\Psi^{(0)}|\hat{H}|\hat{a}_{i,\sigma}\Psi^{(0)}\rangle + E_0 \qquad \varepsilon_a = \langle \hat{a}^\dagger_{a,\sigma}\Psi^{(0)}|\hat{H}|\hat{a}^\dagger_{a,\sigma}\Psi^{(0)}\rangle - E_0$$

$$\begin{aligned}\hat{H}^D = & \sum_i \varepsilon_i \hat{E}_{ii} + \sum_a \varepsilon_a \hat{E}_{aa} \qquad \longleftarrow \qquad \text{HF-type Fock operator contribution}\\ & + \left(2\sum_i h_{ii} + \sum_{i,j}\Big(2\langle ij|ij\rangle - \langle ij|ji\rangle\Big)\right) - 2\sum_i \varepsilon_i \\ & + \sum_{uv}\left(h_{uv} + \sum_i \Big(2\langle ui|vi\rangle - \langle ui|iv\rangle\Big)\right)\hat{E}_{uv} + \frac{1}{2}\sum_{uvwx}\langle uw|vx\rangle\Big(\hat{E}_{uv}\hat{E}_{wx} - \delta_{vw}\hat{E}_{ux}\Big)\end{aligned}$$

- $\hat{H}^D|\Psi^{(0)}\rangle = \hat{H}^{\text{CAS}}|\Psi^{(0)}\rangle = E_0|\Psi^{(0)}\rangle$

- When $\Psi^{(0)}$ reduces to the HF determinant Φ_0, ε_i and ε_a equal the usual canonical HF orbital energies (Koopmans theorem) and Dyall's Hamiltonian reduces to the (shifted) Fock operator

$$\hat{H}^D \quad \longrightarrow \quad \hat{F} + E_{\text{HF}} - 2\sum_i \varepsilon_i = \hat{F}^D$$

- Double contraction: keep one perturber per excitation subspace. For example in $S_{ab}^{(-2)}$

$$\{\hat{E}_{au}\hat{E}_{bv}|\Psi^{(0)}\rangle\}_{uv} \qquad \longrightarrow \qquad \Psi_{ab}^{(-2)} = \sum_{uv} C_{ab,uv}^{(-2)}\hat{E}_{au}\hat{E}_{bv}|\Psi^{(0)}\rangle$$

contracted **strongly contracted**

- Advantage: the number of perturbers is reduced and they are now orthonormal.

- Choice of the $C_{ab,uv}^{(-2)}$ coefficients: analogy with a contracted formulation of MP2.

EX10: Show that $\hat{H}|\Phi_0\rangle$ projected onto the doubly-excited determinants can be rewritten as

$$\sum_{D}|D\rangle\langle D|\hat{H}|\Phi_0\rangle = \frac{1}{2}\sum_{a,b,i,j}\langle ab|ij\rangle\hat{E}_{ai}\hat{E}_{bj}|\Phi_0\rangle = \sum_{a\leq b}\sum_{i\leq j}|\Psi_{ij,ab}^{(0)}\rangle$$

where $$|\Psi_{ij,ab}^{(0)}\rangle = \hat{P}_{S_{ij,ab}^{(0)}}\hat{H}|\Phi_0\rangle$$

$$= (1-\frac{1}{2}\delta_{ij})(1-\frac{1}{2}\delta_{ab})\Big(\langle ab|ij\rangle\hat{E}_{ai}\hat{E}_{bj} + \langle ab|ji\rangle\hat{E}_{bi}\hat{E}_{aj}\Big)|\Phi_0\rangle$$

EX11: The purpose of this exercise is to show that MP2 can be rewritten in a contracted form, using the perturber wave functions $\Psi^{(0)}_{ij,ab}$ and the shifted Fock operator $\hat{F}^D$.

(i) Prove that the square norm of $\Psi^{(0)}_{ij,ab}$ equals

$$N^{(0)}_{ij,ab} = \langle \Psi^{(0)}_{ij,ab} | \Psi^{(0)}_{ij,ab} \rangle = 4(1-\frac{1}{2}\delta_{ij})(1-\frac{1}{2}\delta_{ab})\Big(\langle ab|ij\rangle^2 + \langle ab|ji\rangle^2 - \langle ab|ij\rangle\langle ab|ji\rangle\Big)$$

(ii) The unperturbed Hamiltonian in the contracted MP2 is defined as

$$\hat{H}_0 = \langle \Phi_0 | \hat{F}^D | \Phi_0 \rangle |\Phi_0\rangle\langle\Phi_0| + \sum_{a\leq b}\sum_{i\leq j} \frac{\langle \Psi^{(0)}_{ij,ab} | \hat{F}^D | \Psi^{(0)}_{ij,ab} \rangle}{N^{(0)}_{ij,ab}} \frac{|\Psi^{(0)}_{ij,ab}\rangle\langle\Psi^{(0)}_{ij,ab}|}{N^{(0)}_{ij,ab}}$$

Show that the first- and second-order corrections to the energy equal

$$E^{(1)} = 0 \qquad \text{and} \qquad E^{(2)} = \sum_{a\leq b}\sum_{i\leq j} \frac{N^{(0)}_{ij,ab}}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

(iii) Conclude that the standard MP2 energy expression is thus recovered through second order.

Strongly Contracted NEVPT2

- Perturber wave functions: $|\Psi_l^{(k)}\rangle = \hat{P}_{S_l^{(k)}} \hat{H} |\Psi^{(0)}\rangle, \qquad N_l^{(k)} = \langle \Psi_l^{(k)} | \Psi_l^{(k)} \rangle$

- Unperturbed Hamiltonian:

$$\hat{H}_0 = E_0 |\Psi^{(0)}\rangle\langle\Psi^{(0)}| + \sum_{k,l} \frac{E_l^{(k)}}{N_l^{(k)}} |\Psi_l^{(k)}\rangle\langle\Psi_l^{(k)}|, \qquad E_l^{(k)} = \frac{\langle \Psi_l^{(k)} | \hat{H}^D | \Psi_l^{(k)} \rangle}{N_l^{(k)}}$$

- First and second-order energy corrections:

$$E^{(1)} = 0 \quad \text{and} \quad E^{(2)} = \sum_{k,l} \frac{1}{N_l^{(k)}} \frac{\langle \Psi_l^{(k)} | \hat{H} | \Psi^{(0)} \rangle^2}{E_0 - E_l^{(k)}} = \sum_{k,l} \frac{N_l^{(k)}}{E_0 - E_l^{(k)}}$$

- Explicit expressions for the zeroth-order energies:

$$\hat{H}^D = \hat{F}^D + {}^A\hat{H}^D, \qquad {}^A\hat{H}^D = \sum_{uv} \left(h_{uv} + \sum_i \Big(2\langle ui|vi\rangle - \langle ui|iv\rangle \Big) \right) \hat{E}_{uv}$$
$$+ \frac{1}{2} \sum_{uvwx} \langle uw|vx\rangle \Big(\hat{E}_{uv}\hat{E}_{wx} - \delta_{vw}\hat{E}_{ux} \Big)$$

$$N_l^{(k)} E_l^{(k)} = \langle \Psi_l^{(k)} | \hat{H}^D \hat{P}_{S_l^{(k)}} \hat{H} | \Psi^{(0)} \rangle = \langle \Psi_l^{(k)} | [\hat{H}^D, \hat{P}_{S_l^{(k)}} \hat{H}] | \Psi^{(0)} \rangle + \langle \Psi_l^{(k)} | \hat{P}_{S_l^{(k)}} \hat{H} \underbrace{\hat{H}^D | \Psi^{(0)} \rangle}_{E_0 |\Psi^{(0)}\rangle}$$

$$= \langle \Psi_l^{(k)} | [\hat{H}^D, \hat{P}_{S_l^{(k)}} \hat{H}] | \Psi^{(0)} \rangle + E_0 N_l^{(k)}$$

the denominators in the NEVPT2 energy expansion thus become

$$E_0 - E_l^{(k)} = -\frac{1}{N_l^{(k)}} \langle \Psi_l^{(k)} | [\hat{H}^D, \hat{P}_{S_l^{(k)}} \hat{H}] | \Psi^{(0)} \rangle$$

$$= -\frac{1}{N_l^{(k)}} \langle \Psi_l^{(k)} | [\hat{F}^D, \hat{P}_{S_l^{(k)}} \hat{H}] | \Psi^{(0)} \rangle - \frac{1}{N_l^{(k)}} \langle \Psi_l^{(k)} | [{}^A\hat{H}^D, \hat{P}_{S_l^{(k)}} \hat{H}] | \Psi^{(0)} \rangle$$

- $\underline{S_{ij,ab}^{(0)} \text{ subspace:}}$

$$[\hat{F}^D, \hat{P}_{S_{ij,ab}^{(0)}} \hat{H}] | \Psi^{(0)} \rangle = (\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j) \, |\Psi_{ij,ab}^{(0)}\rangle, \qquad [{}^A\hat{H}^D, \hat{P}_{S_{ij,ab}^{(0)}} \hat{H}] | \Psi^{(0)} \rangle = 0$$

$$E_0 - E_{ij,ab}^{(0)} = \varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b \qquad \longleftarrow \qquad \text{MP2-type denominator}$$

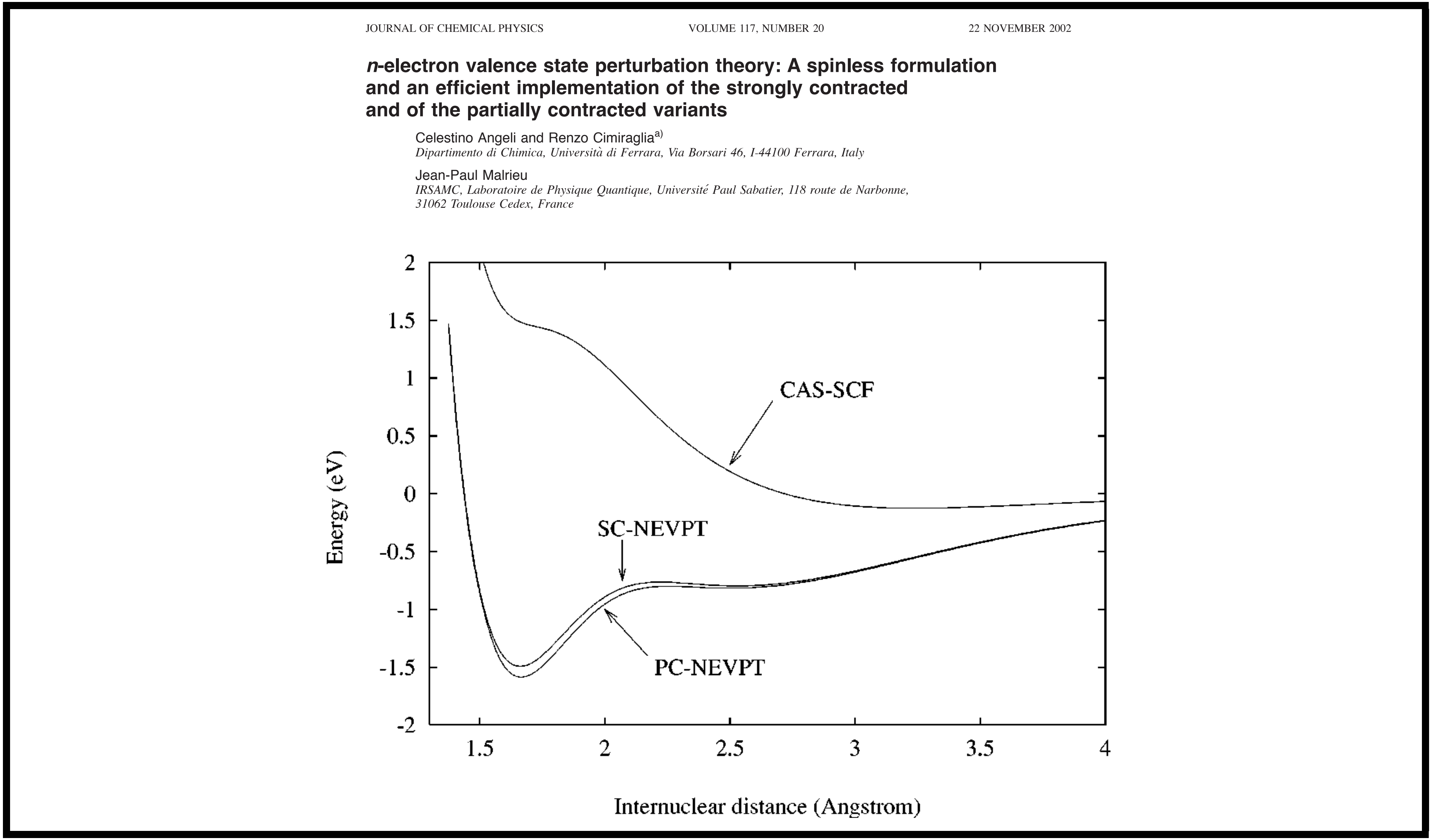
- $S^{(+1)}_{ij,a}$ subspace:

$$[\hat{F}^D, \hat{P}_{S^{(+1)}_{ij,a}} \hat{H}]|\Psi^{(0)}\rangle = (\varepsilon_a - \varepsilon_i - \varepsilon_j)\,|\Psi^{(+1)}_{ij,a}\rangle, \qquad [{}^{A}\hat{H}^{D}, \hat{P}_{S^{(+1)}_{ij,a}} \hat{H}]|\Psi^{(0)}\rangle \neq 0$$

$$\varepsilon^{(+1)}_{ij,a} = \frac{1}{N^{(+1)}_{ij,a}} \langle\Psi^{(+1)}_{ij,a}|[{}^{A}\hat{H}^{D}, \hat{P}_{S^{(+1)}_{ij,a}} \hat{H}]|\Psi^{(0)}\rangle \qquad \longleftarrow$$

effective one-electron energy

$$\boxed{E_0 - E^{(+1)}_{ij,a} = \varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon^{(+1)}_{ij,a}}$$

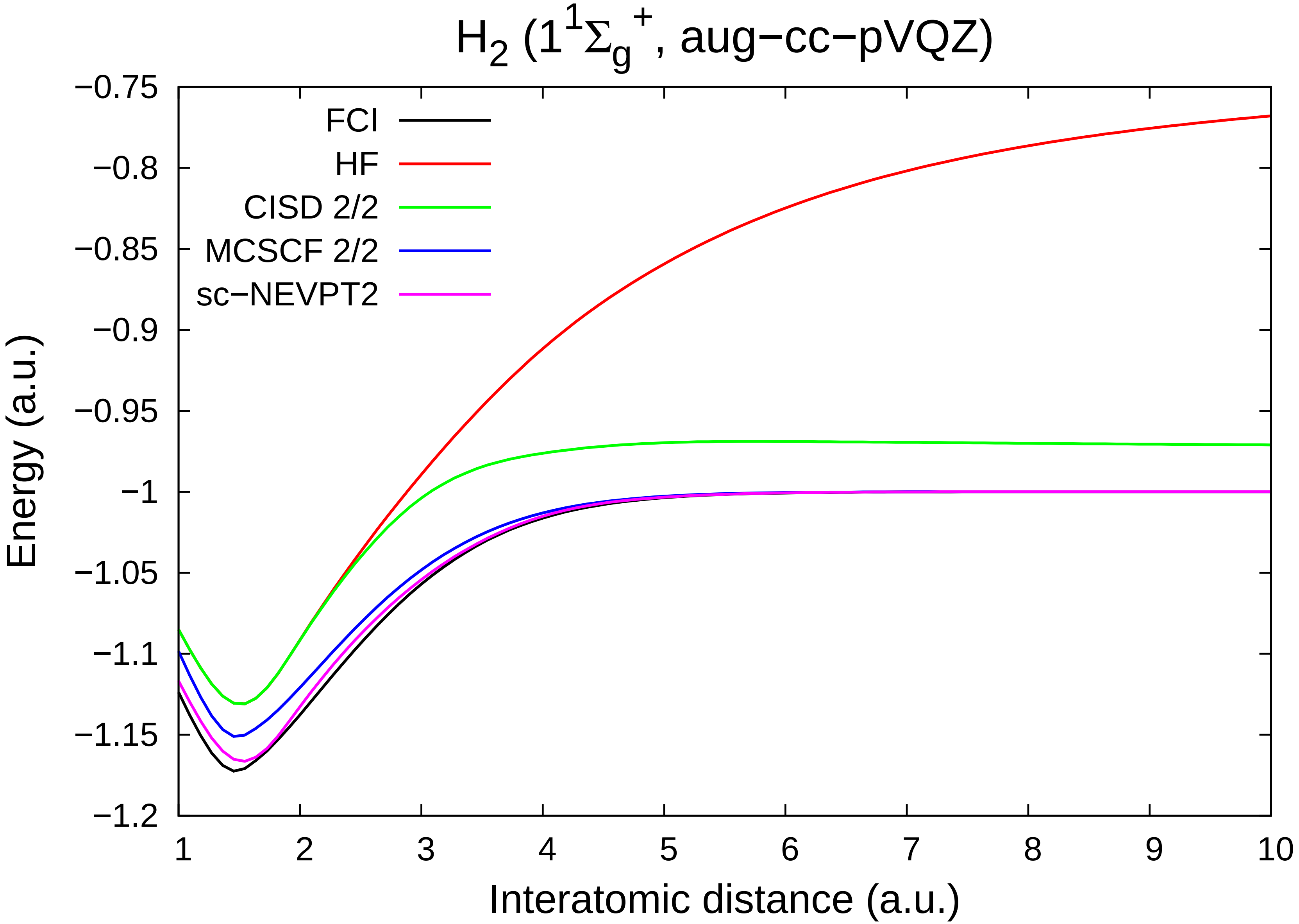


JOURNAL OF CHEMICAL PHYSICS VOLUME 117, NUMBER 20 22 NOVEMBER 2002

n-electron valence state perturbation theory: A spinless formulation and an efficient implementation of the strongly contracted and of the partially contracted variants

Celestino Angeli and Renzo Cimiraglia[a)]
Dipartimento di Chimica, Università di Ferrara, Via Borsari 46, I-44100 Ferrara, Italy

Jean-Paul Malrieu
IRSAMC, Laboratoire de Physique Quantique, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex, France


H_2 ($1^1\Sigma_g^+$, aug−cc−pVQZ)
FCI
HF
CISD 2/2
MCSCF 2/2
sc−NEVPT2
Energy (a.u.)
−0.75
−0.8
−0.85
−0.9
−0.95
−1
−1.05
−1.1
−1.15
−1.2
1
2
3
4
5
6
7
8
9
10
Interatomic distance (a.u.)

Non-perturbative post-MCSCF models

- Multi-Reference CI (MRCI):

$$|\Psi(\mathbf{C}_1,\ldots,\mathbf{C}_i,\ldots)\rangle = \sum_i \left(C_{0,i}|i\rangle + \sum_S C_{S,i}\hat{S}|i\rangle + \sum_D C_{D,i}\hat{D}|i\rangle + \ldots \right)$$

where the CI coefficients $C_{0,i}, C_{S,i}, C_{D,i}, \ldots$ are optimized variationally.

In the so-called "internally contracted formulation", the number of CI coefficients to be optimized is reduced as follows

$$\mathbf{C}_i = \mathbf{C}C_i^{(0)}, \qquad C_i^{(0)}\text{: CI coefficients optimized at the MCSCF level}$$

$$\longrightarrow \quad |\Psi(\mathbf{C})\rangle = C_0|\Psi^{(0)}\rangle + \sum_S C_S\hat{S}|\Psi^{(0)}\rangle + \sum_D C_D\hat{D}|\Psi^{(0)}\rangle + \ldots$$

MRCI is accurate for small molecules but it has size-consistency problems and it is less and less practical for large molecular systems.

Non-perturbative post-MCSCF models

- Multi-Reference CC (MRCC):

$$|\Psi(\mathbf{t}_1,\ldots,\mathbf{t}_i,\ldots)\rangle = \sum_i C_i\, e^{\hat{\mathcal{T}}_i}|i\rangle \qquad \longleftarrow \qquad \text{state universal formulation}$$

In the internally contracted formulation

$$\hat{\mathcal{T}}_i = \hat{\mathcal{T}} \quad \text{and} \quad C_i = C_i^{(0)}$$

$$\longrightarrow \qquad |\Psi(\mathbf{t})\rangle = e^{\hat{\mathcal{T}}}|\Psi^{(0)}\rangle$$

Problem: the BCH expansion does not truncate !

`http://junq.info/?s=multireference+coupled+cluster&searchsubmit=&lang=en`

Post-HF quantum chemistry for excited states

- Time-dependent response theory: $\hat{H}(t) = \hat{H} + \varepsilon\hat{V}\cos(\omega t)$

$$\hat{H}(t)|\Psi(t)\rangle = \mathrm{i}\frac{d}{dt}|\Psi(t)\rangle \quad \longrightarrow \quad \hat{H}(t)|\tilde{\Psi}(t)\rangle - \mathrm{i}\frac{d}{dt}|\tilde{\Psi}(t)\rangle = Q(t)|\tilde{\Psi}(t)\rangle$$

where $|\tilde{\Psi}(t)\rangle = e^{+\mathrm{i}\int_{t_0}^{t} Q(t)dt}|\Psi(t)\rangle, \qquad \frac{d}{dt}|\tilde{\Psi}(t)\rangle = 0$ when $\varepsilon = 0$

- $Q(t) = \langle\tilde{\Psi}(t)|\hat{H}(t) - \mathrm{i}\frac{d}{dt}|\tilde{\Psi}(t)\rangle$ is referred to as time-dependent quasienergy
- $Q = \int_{t_0}^{t_1} Q(t)dt$ is simply referred to as quasienergy
- The exact time-dependent wave function $\tilde{\Psi}(t)$ can be obtained in two ways:

$\forall\varepsilon$

variational formulation	**non-variational formulation**
$\delta Q = 0$	$\hat{H}(t)\|\tilde{\Psi}(t)\rangle - \mathrm{i}\frac{d}{dt}\|\tilde{\Psi}(t)\rangle = Q(t)\|\tilde{\Psi}(t)\rangle$

Post-HF quantum chemistry for excited states

- Approximate parametrized time-dependent wave function: $\tilde{\Psi}(\boldsymbol{\lambda}(t))$

- Linear response: $\boldsymbol{\lambda}(t) = \underbrace{\left.\frac{\partial \boldsymbol{\lambda}(t)}{\partial \varepsilon}\right|_0}\varepsilon + \ldots$

$$\downarrow$$

poles → excitation energies

- Linear response equations for variational methods (TD-HF, TD-MCSCF)

$$\left.\frac{d}{d\varepsilon}\delta Q\right|_0 = 0$$

- Linear response equations for non-variational methods (like CC) can be obtained from the (CC) quasienergy expression to which conditions (CC equations) scaled by Lagrange multipliers are added.

Post-HF quantum chemistry for excited states

- State-averaged MCSCF model: simultaneous optimization of the ground and the lowest $n-1$ excited states at the MCSCF level.

- Iterative procedure: n initial orthonormal states are built from the same set of orbitals.

$$|\Psi_I^{(0)}\rangle = \sum_i C_{I,i}^{(0)}\,|i\rangle, \qquad\qquad I = 1,\ldots,n$$

- Double exponential parametrization:

$$\boxed{|\Psi_I(\boldsymbol{\kappa},\mathbf{S})\rangle = e^{-\hat{\kappa}}\,e^{-\hat{S}}|\Psi_I^{(0)}\rangle} \qquad \text{where} \qquad \hat{S} = \sum_{J=1}^{n}\sum_{K>J} S_{KJ}\Big(|\Psi_K^{(0)}\rangle\langle\Psi_J^{(0)}| - |\Psi_J^{(0)}\rangle\langle\Psi_K^{(0)}|\Big)$$

and $\displaystyle\sum_i |i\rangle\langle i| = \sum_K |\Psi_K^{(0)}\rangle\langle\Psi_K^{(0)}|$

Post-HF quantum chemistry for excited states

- State-averaged energy: $E(\boldsymbol{\kappa}, \mathbf{S}) = \sum_{I=1}^{n} w_I \langle \Psi_I(\boldsymbol{\kappa}, \mathbf{S}) | \hat{H} | \Psi_I(\boldsymbol{\kappa}, \mathbf{S}) \rangle$

  where w_I are arbitrary weights. In the so-called "equal weight" state-averaged MCSCF calculation $w_I = \frac{1}{n}$.

- Variational optimization: $\frac{\partial E(\boldsymbol{\kappa}, \mathbf{S})}{\partial \boldsymbol{\kappa}} = \frac{\partial E(\boldsymbol{\kappa}, \mathbf{S})}{\partial \mathbf{S}} = 0$

- Short-range dynamical correlation can then be recovered, for example, at the Multi-State CASPT2 or NEVPT2 levels.

Summary and outlook

- Post-HF methods are as various as electron correlation effects
- They are usually split into two types: single- and multi-reference methods
- Single-reference methods are used for modeling short-range and long-range dynamical correlation: the state-of-the-art method is Coupled Cluster
- The description of the Coulomb hole is significantly improved when using explicitly correlated methods (faster convergence with respect to the basis set).
- Multi-reference methods describe both static and dynamical correlations (multiconfigurational systems).
- The multi-reference extension of single-reference methods is neither obvious nor unique. It is still a challenging area.

Summary and outlook

- High accuracy in wave function theory usually means high computational cost. Current developments: parallelization, atomic-orbital-based formulations (linear scaling), density-fitting (two-electron integrals), ...
- In this respect DFT is much more appealing to chemists and physicists
- Kohn-Sham DFT is a single-reference method which should be able, in its exact formulation, to describe multiconfigurational systems
- Standard approximate exchange-correlation functionals cannot treat adequately static correlation
- The development of rigorous hybrid MCSCF-DFT models is promising but still quite challenging.
- Indeed, in wave function theory, the multiconfigurational extension of the HF method is clearly formulated. What the multiconfigurational extension of Kohn-Sham DFT should be is unclear.
- Current developments: DFT based on fictitious partially-interacting systems, ensemble DFT, ...