From planetology to Hopf algebra, a quantum chemistry story

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Deficiencies of spectroscopic databases for planetology - I

"The methane opacity dominates the infrared spectrum of Jupiter and other outer planets. This is readily apparent in the Jovian spectra recorded by the Visible and Infrared Mapping Spectrometer on the Cassini spacecraft. The CH_4 abundances are even greater in the more distant outer planets and Titan." L. R. Brown, J. Quant. Spectrosc. Radiat. Transfer **96**, 251-270 (2005).

However in the latest version of the HITRAN database:

- Only 1% of the 40256 features of methane between 1.1-1.6 and 1.8-2.1 μm are assigned $\Longrightarrow$ one cannot extrapolate the 296K (room temperature) spectra to 50K (typical outer planet atmosphere temperature) or 1000K (typical T-Brown Dwarf temperature)

- Without these lines, error bar on the opacity of T-brown dwarf atmospheres $\Longrightarrow$ factor 2 uncertainty on the age and size of these objects!

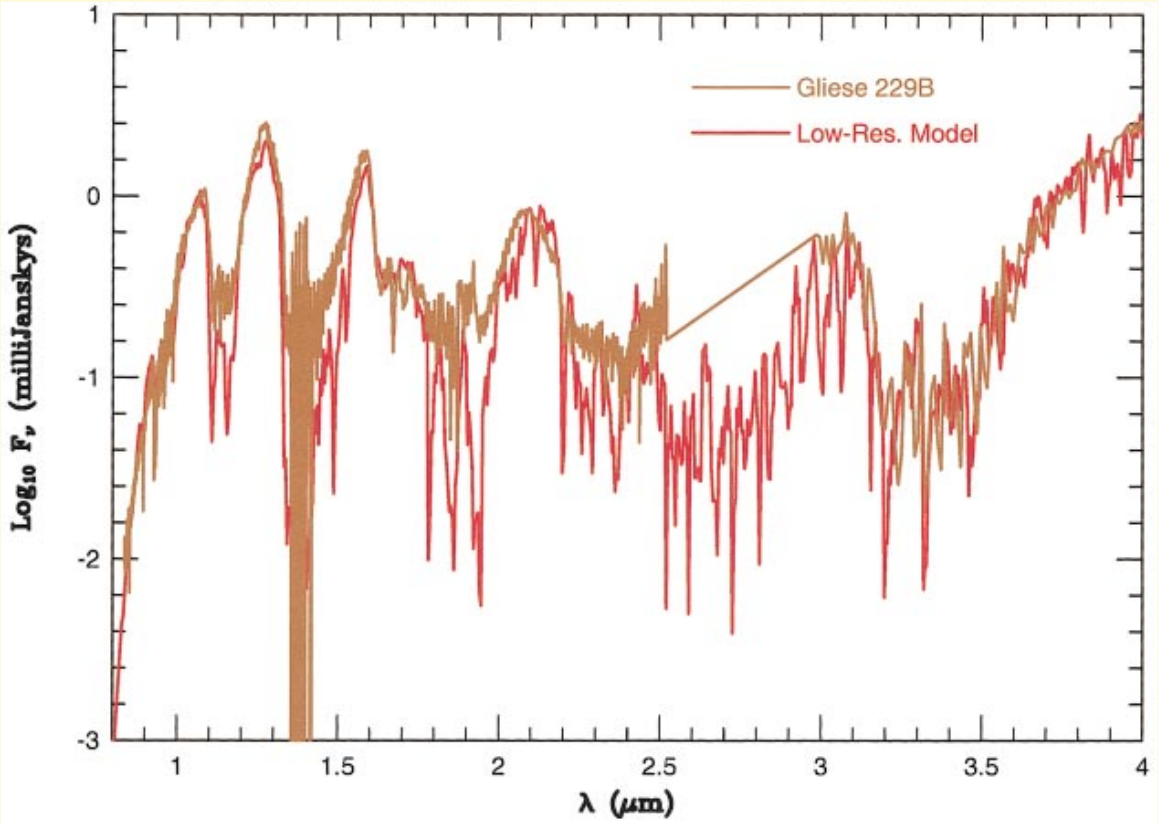
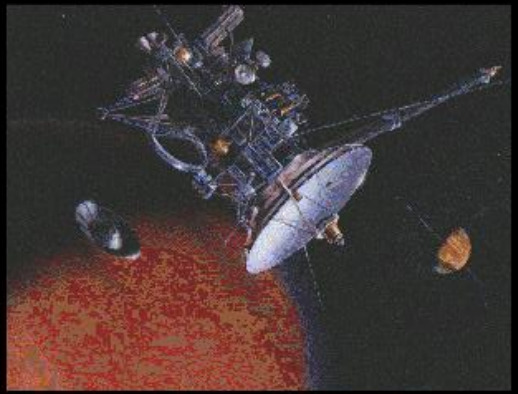
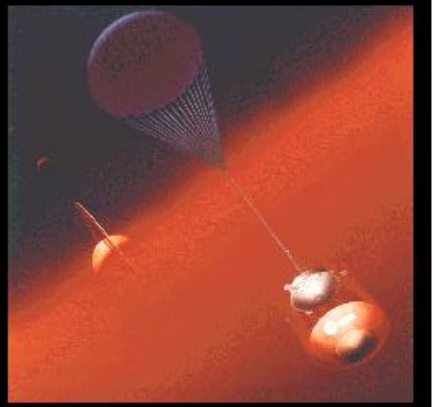


FIG. 17. A comparison of a recently generated (Barrows, unpublished) low-resolution spectral model at T_{eff}=950 K and $g = 10^5$ cm s^{-2} (in red) with the Leggett *et al.* (1999) spectrum of Gliese 229B (in gold). The characteristic spikes at Z, J, H, and K are due to flux streaming through the holes in the water absorption spectrum. The ~1.7- and 3.3-μm bands of methane are readily apparent. This is a generic T dwarf spectrum in the near infrared [Color].

NASA/ESA





Cassini-Huygens
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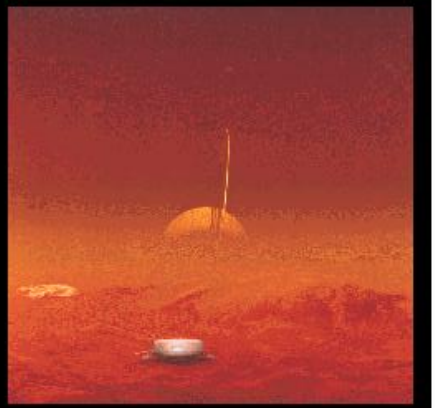
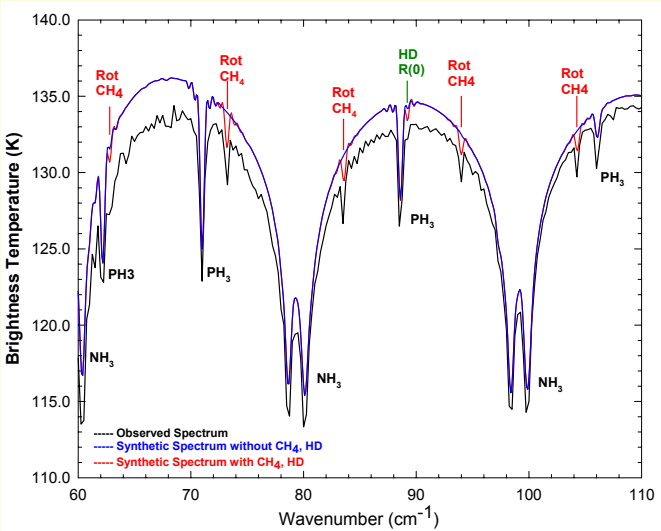


Deficiencies of spectroscopic databases for planetology - II



The far infrared rotational lines of methane have been identified for the first time in Jupiter's atmosphere by the Cassini mission. HITRAN far infrared line parameters are not compatible with the observations.

Can *ab initio* quantum chemistry calculations fill the gaps?

Basic molecular rotation theory

$$H_{rigid} = A\Pi_{x'}^2 + B\Pi_{y'}^2 + C\Pi_{z'}^2$$

where $\vec{\Pi}$ is the total angular momentum, A, B, C, are the "rotational constants" (depend on the equilibrium geometry and nuclear masses).

- Ex: Spherical top $A = B = C$

$$H_{rigid} = A\|\Pi\|^2$$

Eigenvalues: $A\ J(J+1),\ J = 0, \ldots, \infty$

- Ex: Symmetrical top $A = B \neq C$

$$H_{rigid} = A\|\Pi\|^2 + (C - A)\Pi_z^2$$

Eigenvalues: $AJ(J+1) + (C-A)k^2,\ J = 0, \ldots, \infty,\ k = -J, \ldots, +J$

1. Calculation of Rotational Spectra

$$H(X,Y) = H_0(X) + \varepsilon H_1(X,Y)$$

where, $X = [(Q_i)_i, (P_k)_k]$, and Y, denotes the Euler angles in the Eckart frame and their conjugate momenta.

$$H_0(X) = \tfrac{1}{2}\vec{P}^T \cdot \vec{P} + V_{BO} - \tfrac{1}{8}\, Tr\,(\mu) + \tfrac{1}{2}\, \vec{\pi}^T\, \mu\, \vec{\pi}$$

$$\varepsilon H_1(X,Y) = \tfrac{1}{2}\, (\vec{\Pi} - 2\vec{\pi})^T\, \mu\, \vec{\Pi}$$

Rayleigh-Schrödinger perturbation theory ...

$$H(\varphi_0 + \varepsilon\psi_1 + \varepsilon^2\psi_2 + \cdots) = (\lambda_0 + \varepsilon\lambda_1 + \varepsilon^2\lambda_2 + \cdots).(\varphi_0 + \varepsilon\psi_1 + \varepsilon^2\psi_2 + \cdots)$$

. . . generalised for a module over a non-commutative ring

- $A = \sum_{n_x,n_y,n_z} \mathbb{C}\ \Pi_x^{n_x}\ \Pi_y^{n_y}\ \Pi_z^{n_z}$
- $\forall\ i \neq 0,\ \varepsilon^i\ \lambda_i\ \in\ A$
- $\forall\ i \neq 0,\ \varepsilon^i\ \psi_i = \sum_k a_k\ \varphi_k$ where the $(\varphi_k)_k$ are the eigenfunctions of H_0 associated to the eigenvalues $(\mu_k)_k$ and the $(a_k)_k$ are elements of the ring A.

$$\lambda_0 = \mu_0,$$

$$\varepsilon^1\ \lambda_1 = \langle\varphi_0|\varepsilon H_1|\varphi_0\rangle,$$

$$\varepsilon^2\ \lambda_2 = \sum_{k\neq 0} \frac{\langle\varphi_0|\varepsilon H_1|\varphi_k\rangle\langle\varphi_k|\varepsilon H_1|\varphi_0\rangle}{\mu_0 - \mu_k},$$

$$\varepsilon^3\ \lambda_3 \;=\; \sum_{k,k'\neq 0} \frac{\langle\varphi_0|\varepsilon H_1|\varphi_k\rangle\langle\varphi_k|\varepsilon H_1|\varphi_{k'}\rangle\langle\varphi_{k'}|\varepsilon H_1|\varphi_0\rangle}{(\mu_0-\mu_k)(\mu_0-\mu_{k'})} - \sum_{k\neq 0} \frac{\langle\varphi_0|\varepsilon H_1|\varphi_k\rangle\langle\varphi_0|\varepsilon H_1|\varphi_0\rangle\langle\varphi_k|\varepsilon H_1|\varphi_0\rangle}{(\mu_0-\mu_k)^2},$$

$$\begin{aligned}\varepsilon^4\ \lambda_4 \;=\; & \sum_{k,k',k"\neq 0} \frac{\langle\varphi_0|\varepsilon H_1|\varphi_k\rangle\langle\varphi_k|\varepsilon H_1|\varphi_{k'}\rangle\langle\varphi_{k'}|\varepsilon H_1|\varphi_{k"}\rangle\langle\varphi_{k"}|\varepsilon H_1|\varphi_0\rangle}{(\mu_0-\mu_k)(\mu_0-\mu_{k'})(\mu_0-\mu_{k"})} \\ & - \sum_{k,k'\neq 0} \frac{\langle\varphi_0|\varepsilon H_1|\varphi_k\rangle\langle\varphi_k|\varepsilon H_1|\varphi_{k'}\rangle\langle\varphi_0|\varepsilon H_1|\varphi_0\rangle\langle\varphi_{k'}|\varepsilon H_1|\varphi_0\rangle}{(\mu_0-\mu_k)(\mu_0-\mu_{k'})^2} \\ & - \sum_{k,k'\neq 0} \frac{\langle\varphi_0|\varepsilon H_1|\varphi_k\rangle\langle\varphi_0|\varepsilon H_1|\varphi_0\rangle\langle\varphi_k|\varepsilon H_1|\varphi_{k'}\rangle\langle\varphi_{k'}|\varepsilon H_1|\varphi_0\rangle}{(\mu_0-\mu_k)^2(\mu_0-\mu_{k'})} \\ & - \sum_{k,k'\neq 0} \frac{\langle\varphi_0|\varepsilon H_1|\varphi_k\rangle\langle\varphi_0|\varepsilon H_1|\varphi_{k'}\rangle\langle\varphi_{k'}|\varepsilon H_1|\varphi_0\rangle\langle\varphi_k|\varepsilon H_1|\varphi_0\rangle}{(\mu_0-\mu_k)^2(\mu_0-\mu'_k)} \\ & + \sum_{k\neq 0} \frac{\langle\varphi_0|\varepsilon H_1|\varphi_k\rangle\langle\varphi_0|\varepsilon H_1|\varphi_0\rangle^2\langle\varphi_k|\varepsilon H_1|\varphi_0\rangle}{(\mu_0-\mu_k)^3}.\end{aligned}$$

Speed of convergence with the order of the perturbation

Energies in cm^{-1} of methane rotational levels in its vibrational ground state

	Van Vleck Perturbation[a]			Our method[b]			STDS[c]
	ord2	ord4	ord6	ord0	ord2	ord4	
$J=1$	10.59973	10.44174	10.44237	10.63296	10.48010	10.48008	10.481648
$J=2$	31.79918	31.32521	31.32439	31.89887	31.43746	31.43742	31.442121
	31.79918	31.32521	31.32463	31.89887	31.43772	31.43769	31.442387
$J=3$	63.59837	62.65041	62.64064	63.79775	62.86645	62.86635	62.875779
	63.59837	62.65041	62.64162	63.79775	62.86749	62.86742	62.876841
	63.59837	62.65041	62.64285	63.79775	62.86879	62.86877	62.878169

[a] X. G. Wang et E. L. Sibert, Spectrochimica Acta A, **58** (2002) 863. 12 force constants adjusted on experiment.

[b] P. Cassam-Chenaï and J. Liévin, Int. J. Quantum Chem. **93**, 245-264 (2003). Purely *ab initio* results.

[c] C. Wenger and J. P. Champion, J. Quant. Spectrosc. Radiat. Transfer **59**, 471-480 (1998). From an effective Hamiltonian accurate to 10^{-5} cm^{-1} .

Energies in cm^{-1} of methane rotational levels in its vibrational ground state

	Carter/Bowman[a]	Wang/Carrington[b]	Wang/Sibert[c]	Cassam-Chenaï/Liévin[d]	Exp.[e]
$J=1$	10.47	10.430	10.44237	10.48165	10.481648
$J=2$	N/A	N/A	31.32439	31.44213	31.442121
	N/A	N/A	31.32463	31.44240	31.442387
$J=3$	N/A	N/A	62.64064	62.87581	62.875779
	N/A	N/A	62.64162	62.87689	62.876841
	N/A	N/A	62.64285	62.87824	62.878169
$J=4-18$	N/A	N/A	N/A	largest relative difference 2.10^{-5}	

[a] S. Carter et J. M. Bowman, J. Phys. Chem. **A104**, 2355 (2000). MULTIMODE using Lee, Martin and Taylor PES.

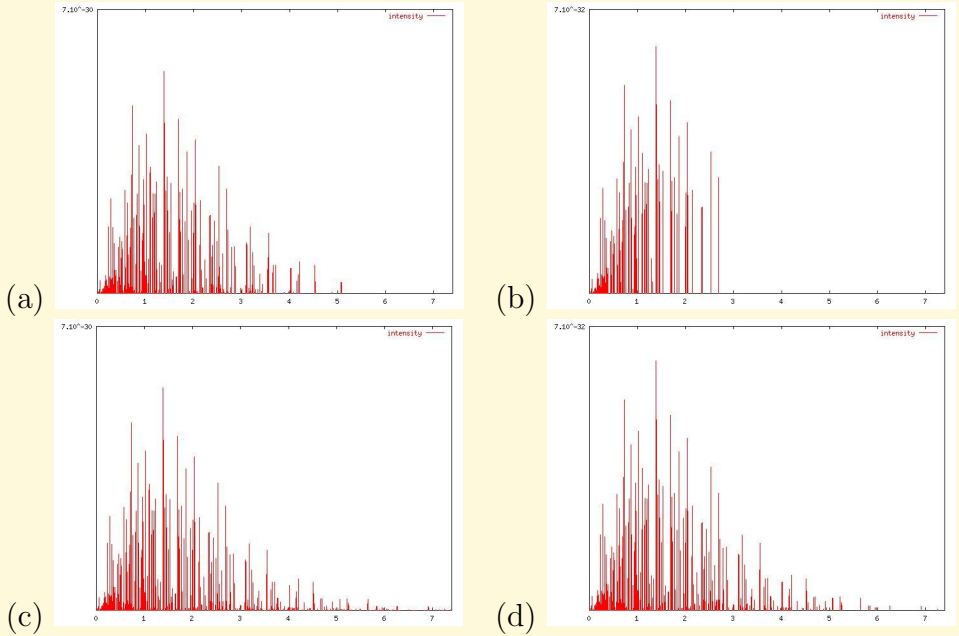
[b] X. G. Wang et T. Carrington,J. Chem. Phys **121**, 2937 (2004). CI calculation using Schwenke PES.

[c] X. G. Wang et E. L. Sibert, Spectrochimica Acta A **58**, 863 (2002). 12 force constants adjusted on experiment.

[d] P. Cassam-Chenaï and J. Liévin, Int. J. Quantum Chem. **93**, 245-264 (2003). VMFCI using Lee, Martin and Taylor PES + generalised perturbation with 1 parameter related to the equilibrium distance scaled by a factor 1.0002535.

[e] C. Wenger and J. P. Champion, J. Quant. Spectrosc. Radiat. Transfer **59**, 471-480 (1998). From an effective Hamiltonian accurate to 10^{-5} cm^{-1} .

Comparison with HITRAN at 500K



P. Cassam-Chenaï, J. Quant. Spectrosc. Radiat. Transfer **82**, 251-277 (2003).

Q-Branch of the vibrational ground state of methane at 500K.
Comparison of the extrapolation from HITRAN for $^{12}CH_4$ (a) and $^{13}CH_4$ (b) with *ab initio* calculated spectra for $^{12}CH_4$ (c) and $^{13}CH_4$ (d). Units as in HITRAN, intensities in [cm^{-1} / (molecule . cm^{-2})], wave numbers in cm^{-1} . Isotopic abundances: 0.988274 for $^{12}CH_4$, 0.0111031 for $^{13}CH_4$.

Generalized perturbation theory - Open problems:

- Diagrammatic representations?
- Linked cluster theorem?
- Hopf algebra structure of the diagrams?

2. Calculation of Vibrational Spectra

The VMFCI method

$$H = \sum_{i_1} h_1(Q_{i_1}, P_{i_1}) + \sum_{i_1,i_2} h_2(Q_{i_1}, P_{i_1}, Q_{i_2}, P_{i_2}) + \cdots + h_n(Q_1, P_1, Q_2, P_2, \cdots, Q_n, P_n)$$

Consider a partition of the n modes into q sets $I_1, I_2, \cdots, I_q$, of respectively $p_1, p_2, \cdots, p_q$ modes,

$$(I_1, I_2, \cdots, I_q) = (\{i_1^1, i_2^1, \cdots, i_{p_1}^1\}, \{i_1^2, i_2^2, \cdots, i_{p_2}^2\}, \cdots, \{i_1^q, i_2^q, \cdots, i_{p_q}^q\}).$$

For each contraction, I_j, we define a partial Hamiltonian,

$$H_j = \sum_{i_1 \in I_j} h_1(Q_{i_1}, P_{i_1}) + \sum_{\{i_1,i_2\} \subset I_j} h_2(Q_{i_1}, P_{i_1}, Q_{i_2}, P_{i_2}) + \cdots + h_{p_j}(Q_{i_1^j}, P_{i_1^j}, Q_{i_2^j}, P_{i_2^j}, \cdots, Q_{i_{p_j}^j}, P_{i_{p_j}^j}),$$

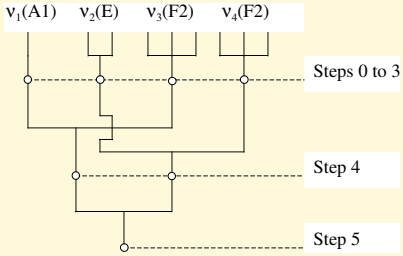
The mean-field equation for I_j is :

$$[H_j + \langle \prod_{I_k \neq I_j} \phi_{V_k}(Q_{i_1^k}, \cdots, Q_{i_{p_k}^k}) | H - H_j | \prod_{I_k \neq I_j} \phi_{V_k}(Q_{i_1^k}, \cdots, Q_{i_{p_k}^k}) \rangle - \epsilon_j] \Phi_j = 0$$

Particular cases

- The partition, $(\{1\}, \{2\}, \cdots, \{n\})$, corresponds to the VSCF method.
- The partition, $(\{1, 2, \cdots, n\})$, corresponds to the VCI method.

General case: example CH_4



VMFCI versus traditional contractions

	Harmonic level	MSP-CI	MSP-VMFCI	MSP-VSCFCI	Converged
ν_4	1345	1356	1295	1318	1309
ν_2	1570	1567	1527	1532	1528
$2\nu_4$	2691	2714	2591	2638	2588
$2\nu_4$	2691	2719	2597	2643	2610
$2\nu_4$	2691	2719	2597	2643	2622
ν_1	3036	3013	2972	2972	2925
ν_3	3157	3214	3176	3062	3027
$2\nu_2$	3141	3131	3051	3061	3051
$2\nu_2$	3141	3134	3054	3064	3054
$3\nu_4$	4036	4079	3896	3966	3868
$3\nu_4$	4036	4087	3905	3974	3905
$3\nu_4$	4036	4088	3905	3974	3915
$3\nu_4$	4036	4088	3906	3974	3929
$3\nu_2$	4711	4694	4573	4588	4573
$3\nu_2$	4711	4699	4579	4594	4579
$3\nu_2$	4711	4699	4579	4594	4579

Wave numbers in cm^{-1} of the vibrational levels of methane calculated for different MSP-methods. MSP-CI goes in the wrong direction for modes 3 and 4 MSP-VSCFCI always go in the right direction and modes 1 and 2 are closer to the converged value than with MSP-CI. (HO modal basis set with quantum number less than 10. Order 0 rotational corrections).

VMFCI - Properties and open problems:

• A minimal symmetry preserving (MSP)-VMFCI converges rapidly and is a good (computationnally cheap) starting point before contracting modes.

• The contraction of resonant modes is necessary and sufficient to tame the resonances which make perturbation methods useless.

• The truncation of high energy states of the previous contraction step when constructing a product basis set for the next step is an efficient way to control the size of the variational space.

• Development of modal basis sets adapted to nuclear motions for which the harmonic approximation is not appropriate?

• Can the same philosophy be adapted to electronic calculations?

3. Calculation of Electronic Spectra

The Configuration Interaction Method (CI)

A CI calculation consists in diagonalising the Hamiltonian matrix $(\langle\Phi_i|H\Phi_j\rangle)_{i,j}$ in a set of orthonormal n-electron functions, $\Phi_1, \ldots, \Phi_m$, or equivalently in finding the stationary points of the energy functionnal $E(\Psi) = \frac{\langle\Psi|H\Psi\rangle}{\langle\Psi|\Psi\rangle}$ in $Span(\Phi_1, \ldots, \Phi_m)$

The Complete Active Space Self-Consistent Field Method (CASSCF)

A CASSCF calculation with p active orbitals (and no frozen core) consists in finding the stationary points of the energy functionnal $E(\Psi) = \frac{\langle\Psi|H\Psi\rangle}{\langle\Psi|\Psi\rangle}$ in $\{\Psi \in \wedge^n\mathcal{H} | \forall\Phi_0, \ldots, \Phi_{p-n} \in \wedge^{n-1}\mathcal{H}, (\Phi_0 \hookleftarrow \Psi) \wedge \cdots \wedge (\Phi_{p-n} \hookleftarrow \Psi) \wedge \Psi = 0\}$.
The case $p = n$ with no spin constraint is the UHF method first developed by Prof. Berthier (and not Pople as found in textbooks).

Variational spaces of traditional methods

$$\Phi = \phi_1^\alpha \Lambda \phi_1^\beta + \beta \phi_1^\alpha \Lambda \phi_2^\beta + \gamma \phi_2^\alpha \Lambda \phi_1^\beta + \delta \phi_2^\alpha \Lambda \phi_2^\beta$$

The three, real, parameters β, γ, δ are considered as independent and varying on $]-\infty, +\infty[$ and an axis is associated with each parameter. In the 3-dimensional space obtained, UHF wave functions satisfy :

$$\beta\gamma = \delta\,,$$

which is clearly the equation of a set of hyperbolae. Singlet wave functions satisfy : $\beta = \gamma$.

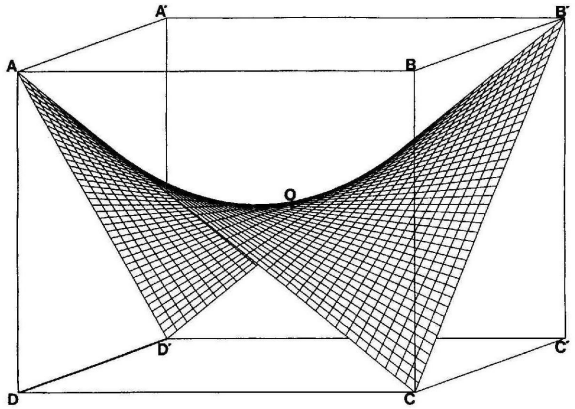


Fig. 1. 2 electrons, 2 orbitals, $S_z = 0$. Each point in the cube corresponds to a multi-configuration, the centre of the cube O being the configuration $\phi_1^\alpha \Lambda \phi_1^\beta$. The volume of the cube is the full unrestricted CI space, the hyperbolic surface ($AOB'CD'$) is the UHF space. The plane ($ADB'C'$) corresponds to the eigenfunctions of $\mathbf{S}^2$ with $S = 0$ (singlet plane). The intersection between the UHF surface and the singlet plane gives the RHF curve (AOB').

The Electronic Mean Field Configuration Interaction method

It consists in constructing successive, approximate, n-electron wave functions of the form:

$$\Psi = \Psi_1 \wedge \cdots \wedge \Psi_r \ ,$$

where $\Psi_i \in \wedge^{n_i}\mathcal{H}$, with $\sum_i n_i = n$, by means of a configuration interaction calculation in a basis set of group functions $\{\Psi_1^i \wedge \Psi_2^0 \wedge \cdots \wedge \Psi_r^0\}_i$ i.e., the wave functions of the first group functions are optimized in the mean field of the ground states of the other groups.

- The process can be iterated by switching to another group until self-consistence is achieved.

- Or/then a coarser partition of the n electron can be selected.

The exterior algebra, $\wedge\mathcal{H}$

Grassmann's exterior product:

$$\begin{array}{rcl} \mathcal{X} : \wedge\mathcal{H} \otimes \wedge\mathcal{H} & \longmapsto & \wedge\mathcal{H} \\ \Phi \otimes \Psi & \longrightarrow & \mathcal{X}(\Phi \otimes \Psi) = \Phi \wedge \Psi \end{array}$$

The fermionic symmetry is built-in in this exterior algebra because of the following antisymmetry relation between exterior products of 1-particle functions:

$$\mathcal{X}(\phi \otimes \psi) = \phi \wedge \psi = -\psi \wedge \phi = -\mathcal{X}(\psi \otimes \phi)$$

which entirely determines the behavior of an n-fermion wave function under the symmetric group $\mathcal{S}_n$. That is to say, for an n-fermion single configuration:

$$\psi_1 \wedge \cdots \wedge \psi_n = (-1)^{|\sigma|} \psi_{\sigma(1)} \wedge \cdots \wedge \psi_{\sigma(n)}$$

The Hopf algebra structure of $\wedge\mathcal{H}$

Exterior coproduct:

$$\begin{aligned} \mathcal{Y} : \wedge\mathcal{H} &\longmapsto \wedge\mathcal{H}\otimes\wedge\mathcal{H} \\ \psi_1\wedge\cdots\wedge\psi_n &\longrightarrow \mathcal{Y}(\psi_1\wedge\cdots\wedge\psi_n) = \sum_{I\in\mathcal{P}_n} \rho_{I,\bar{I}}\psi_{i_1}\wedge\cdots\wedge\psi_{i_p}\otimes\psi_{\bar{i}_1}\wedge\cdots\wedge\psi_{\bar{i}_{n-p}}. \end{aligned}$$

The idea behind the coproduct is to split an n-fermion single configuration function into a p and an $(n-p)$-fermion single configuration functions in all possible ways, where p ranges from 0 to n, the exterior product of the two parts so-obtained giving back the initial function, the sign of the reordering permutation being taken care of.

As an example, let us write down the formula for $\mathcal{Y}$ acting on a 3-fermion configuration,

$$\begin{aligned} \mathcal{Y}(\psi_a\wedge\psi_b\wedge\psi_c) \;=\; & \psi_a\wedge\psi_b\wedge\psi_c\otimes 1 + \psi_a\wedge\psi_b\otimes\psi_c - \psi_a\wedge\psi_c\otimes\psi_b \\ & +\psi_b\wedge\psi_c\otimes\psi_a + \psi_a\otimes\psi_b\wedge\psi_c - \psi_b\otimes\psi_a\wedge\psi_c \\ & +\psi_c\otimes\psi_a\wedge\psi_b + 1\otimes\psi_a\wedge\psi_b\wedge\psi_c. \end{aligned}$$

Hopf algebra fundamental relation

$$\mathcal{Y} \circ \mathcal{X} = (\mathcal{X} \otimes \mathcal{X}) \circ (Id \otimes T \otimes Id) \circ (\mathcal{Y} \otimes \mathcal{Y})$$

where T is the twisting map:

$$\begin{array}{rcl} \forall \Phi \in \wedge^p \mathcal{H} & , & \forall \Psi \in \wedge^q \mathcal{H} \\ T(\Psi \otimes \Phi) & = & (-1)^{pq} \Phi \otimes \Psi. \end{array}$$

The fundamental Hopf algebra relation expresses the fact that the same decomposition of the product of two single configurations into a tensor product of 2 subconfigurations is obtained by applying the coproduct to the exterior product of the two single configurations, or alternatively, by first splitting each single configuration separately ($\mathcal{Y} \otimes \mathcal{Y}$), then grouping the first tensorial components of each decomposition together and the second components together ($Id \otimes T \otimes Id$), and finally by taking the exterior product of the first components on the one hand and the exterior product of the second components on the other hand ($\mathcal{X} \otimes \mathcal{X}$).

Convolution

$$A * B := \mathcal{X} \circ (A \otimes B) \circ \mathcal{Y}.$$

Ex: the Coulomb repulsion between two electrons, $V_{ee} = \frac{1}{||\vec{r_1} - \vec{r_2}||}$, is a 2-electron operator acting on $\wedge^2\mathcal{H}$, the convolution with the identity induces an operator on $\wedge\mathcal{H}$: $V_{ee} * Id$

Iterated products and coproducts

- kth iterated product

$$\mathcal{X}^{[k]} := \mathcal{X} \circ (\mathcal{X}^{[k-1]} \otimes Id) \ ,$$

with $\mathcal{X}^0 = Id$.

- kth iterated coproduct

$$\mathcal{Y}^{[k]} := (Id \otimes \cdots \otimes Id \otimes \mathcal{Y}) \circ \mathcal{Y}^{[k-1]} \ ,$$

We specify further by $\mathcal{Y}^{[k]}_{i_0,\ldots,i_k}$ the component of the iterated coproduct corresponding to the decomposition of an n-Fermion wave function into the tensor product of $(k+1)$ wave functions of $i_0, \ldots, i_k$-particles respectively.

Generalised twist operator

$T^{(p,q)}$, defined on the tensor product of $p.q$, (p and $q > 1$), Fermionic Hilbert spaces, $\wedge^{n_i^j}\mathcal{H}$, with fixed number of particles, n_i^j, $i \in 1, \cdots, p$ and $j \in 1, \cdots, q$.

Let $\Phi := \phi_1^1 \otimes \cdots \otimes \phi_p^1 \otimes \cdots \otimes \phi_1^q \otimes \cdots \otimes \phi_p^q$ be an element of $\wedge^{n_1^1}\mathcal{H} \otimes \cdots \otimes \wedge^{n_p^1}\mathcal{H} \otimes \cdots \otimes \wedge^{n_1^q}\mathcal{H} \otimes \cdots \otimes \wedge^{n_p^q}\mathcal{H}$,

$$T^{(p,q)}[\Phi] = \rho_{n_1^1,\ldots,n_p^1,\ldots,n_1^q,\ldots,n_p^q}\ \phi_1^1 \otimes \cdots \otimes \phi_1^q \otimes \cdots \otimes \phi_p^1 \otimes \cdots \otimes \phi_p^q$$

where $\rho_{n_1^1,\ldots,n_p^1,\ldots,n_1^q,\ldots,n_p^q}$ is the sign of the permutation which would reorder the tensorial components ϕ_i^j in their initial order if we had exterior products in place of tensor products. More explicitely,

$$\rho_{n_1^1,\ldots,n_p^1,\ldots,n_1^q,\ldots,n_p^q} = (-1)^{\sum_{i=1}^{p-1}\sum_{j=2}^{q}\sum_{k=j+1}^{p}\sum_{l=1}^{i-1} n_i^j.n_k^l}.$$

In particular, $Id \otimes T \otimes Id = T^{(2,2)}$.

Generalised Hopf formula

The generalization of the Hopf algebra fundamental relation to the case of iterated product, $\mathcal{X}^{[p-1]}$, $(p > 1)$, and coproduct , $\mathcal{Y}^{[q-1]}$, $(q > 1)$, is,

$$\mathcal{Y}^{[q-1]} \circ \mathcal{X}^{[p-1]} = \underbrace{(\mathcal{X}^{[p-1]} \otimes \cdots \otimes \mathcal{X}^{[p-1]})}_{q factors} \circ T^{(q,p)} \circ \underbrace{(\mathcal{Y}^{[q-1]} \otimes \cdots \otimes \mathcal{Y}^{[q-1]})}_{p factors},$$

or for a particular coproduct component,

$$\mathcal{Y}^{[q-1]}_{n_1,\ldots,n_q} \circ \mathcal{X}^{[p-1]} = \sum_{n_i^j, \sum_{j=1}^{p} n_i^j = n_i} \underbrace{(\mathcal{X}^{[p-1]} \otimes \cdots \otimes \mathcal{X}^{[p-1]})}_{q factors} \circ T^{(q,p)} \circ \underbrace{(\mathcal{Y}^{[q-1]}_{n_1^1,\ldots,n_q^1} \otimes \cdots \otimes \mathcal{Y}^{[q-1]}_{n_1^p,\ldots,n_q^p})}_{p factors}.$$

Laplace formula

$$\langle \mathcal{X}(\Theta \otimes \Phi) | \Psi \rangle \equiv \langle \Theta \wedge \Phi | \Psi \rangle = \langle \Theta \otimes \Phi | \mathcal{Y}(\Psi) \rangle$$

Calculation of matrix elements between group functions

$$\langle \Phi_1 \wedge \Gamma_2 \wedge \cdots \wedge \Gamma_q | (h_2 * Id)[\Psi_1 \wedge \Gamma_2 \wedge \cdots \wedge \Gamma_q] \rangle$$

We set, $\Delta_{q-1} := \Phi_1 \wedge \Gamma_2 \wedge \cdots \wedge \Gamma_{q-1}$, $\Psi := \Psi_1 \wedge \cdots \wedge \Gamma_q$, and re-write the matrix element as:

$$\langle \Delta_{q-1} \wedge \Gamma_q | (h_2 * Id)[\Psi] \rangle =$$
$$\Sigma'_{n_k^l} \langle \Delta_{q-1} \otimes \Gamma_q | (\mathcal{X} \otimes \mathcal{X}) \circ T^{(2,2)} \circ (\mathcal{Y}_{n_1^1, n_2^1} \otimes \mathcal{Y}_{n_1^2, n_2^2}) \circ (h_2 \otimes Id) \circ \mathcal{Y}_{2,n-2}[\Psi] \rangle .$$

The constraints on the summation give rise to at most three terms:

- A term where the n_q-electron integral is an "h_2"-type integral and the $n - n_q$ electron integral is an overlap integral, when $n_1^1 = 0; n_1^2 = n - n_q; n_2^1 = 2; n_2^2 = n_q - 2$, provided that $n_q \geq 2$.
- A term where the n_q-electron integral is an overlap integral and the $n-n_q$ electron integral is a "h_2"-type integral, when $n_1^1 = 2; n_1^2 = n-n_q-2; n_2^1 = 0; n_2^2 = n_q$, provided that $n - n_q \geq 2$.
- A term where the h_2 integral is splitted accross the n_q-electron and the $n-n_q$-electron integrals, when $n_1^1 = 1; n_1^2 = n-n_q-1; n_2^1 = 1; n_2^2 = n_q-1$.

The Electronic MFCI method converges rapidly

Ground state energies in Hartree for LiH
(6-31G*, full core calculations at 3.03642 au)

Step	0	1	2
geminal 1	-7.981090	-8.002268	
geminal 2	-8.001937		-8.003028

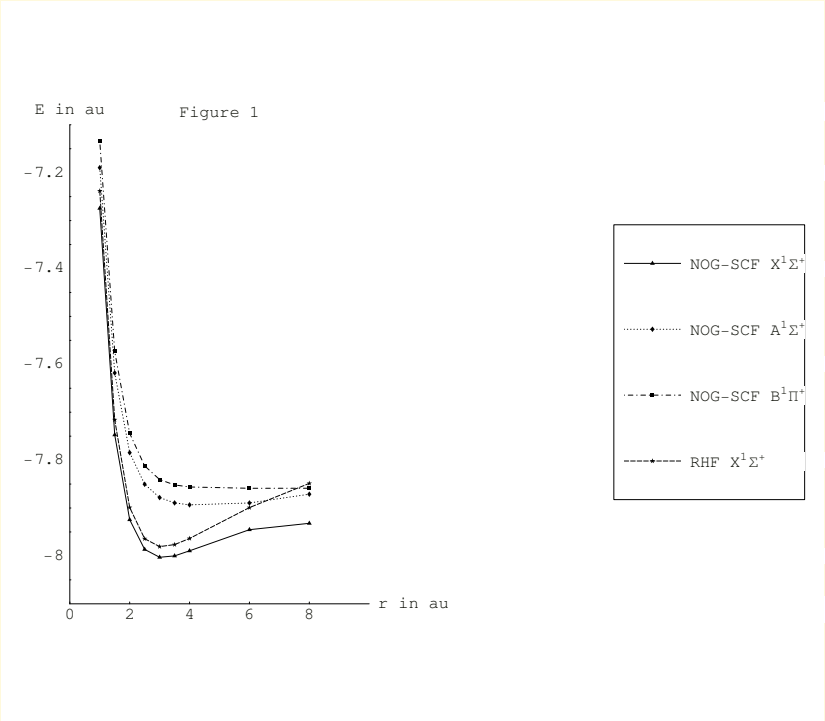
- HF energy: -7.98077 au.
- CCSD(T) energy: -8.00326.
- the antisymmetrized product of strongly orthogonal geminals (APSG) ansatz recovers only 33.5% of the CCSD(T) energy at the scf geometry (i.e. 3.03642 au) for the 6-311G** (5d orbitals) basis (Rosta and Surján, Int. J. Quant. Chem., **80**, p.96, 2000).

Lowest singlet energy levels of Beryllium in Hartree (6-31G*, 6d calculations)

state symmetry	CASPT2 (2 el. 4 orb.)	CASPT2 (4 el. 5 orb.)	Full CI (frozen core, 105 CSFs)	NOG-SCF (239 Coef.)	Full CI (4200 CSFs)
^{1}S	-14.613957	-14.617047	-14.613435	-14.616073	-14.616634
^{1}P	-14.388329	-14.392313	-14.388909	-14.390291	-14.393112
^{1}D	-14.311436	-14.315481	-14.311959	-14.312844	-14.316351
^{1}S			-14.222495	-14.223317	-14.226960
^{1}P			-14.144298	-14.145614	-14.148581
^{1}S			-14.106706	-14.108337	-14.109614
^{1}P			-14.038519	-14.039284	-14.043223
^{1}D			-13.931205	-13.932110	-13.935630
^{1}P			-13.895624	-13.896746	-13.900150
^{1}S			-13.800902	-13.802002	-13.805443

el.: electrons, orb.: orbitals, Coef.: Coefficients, CSFs: Configuration state functions. The CASPT2 results have been communicated to the author by Prof. J. Liévin of the Université Libre de Bruxelles.

The Electronic MFCI method dissociates properly



Performance of geminal-SCF with the number of geminals

Ground state energies in Hartree at 2 au (STO-3G, full core calculations)

Diatomics	LiH	BH	FH
E^0_{RHF}	-7.79355	-24.73706	-98.56156
$E^0_{geminal-SCF}$	-7.81041	-24.78935	-98.60002
E^0_{CISD}	-7.81043	-24.78816	-98.60002
E^0_{CCSD}	-7.81043	-24.78939	-98.60002
$E^0_{CCSD(T)}$	-7.81044	-24.78946	-98.60002

EMFCI - open problems:

- Density of NOG functions in the space of $2n$-electron functions?

- Transformations which leave invariant a group function and preserve its structure?

- Effectiveness of truncation on energy criteria?

- Effectiveness of truncation on p-orthogonality criteria?

- The NOGSCF is already a very fruitful achievement, however completely general EMFCI steps should be implemented