Taming the combinatorics of antisymmetrized product of geminals

Patrick CASSAM-CHENAÏ

Laboratoire J.A. Dieudonné, Nice, France

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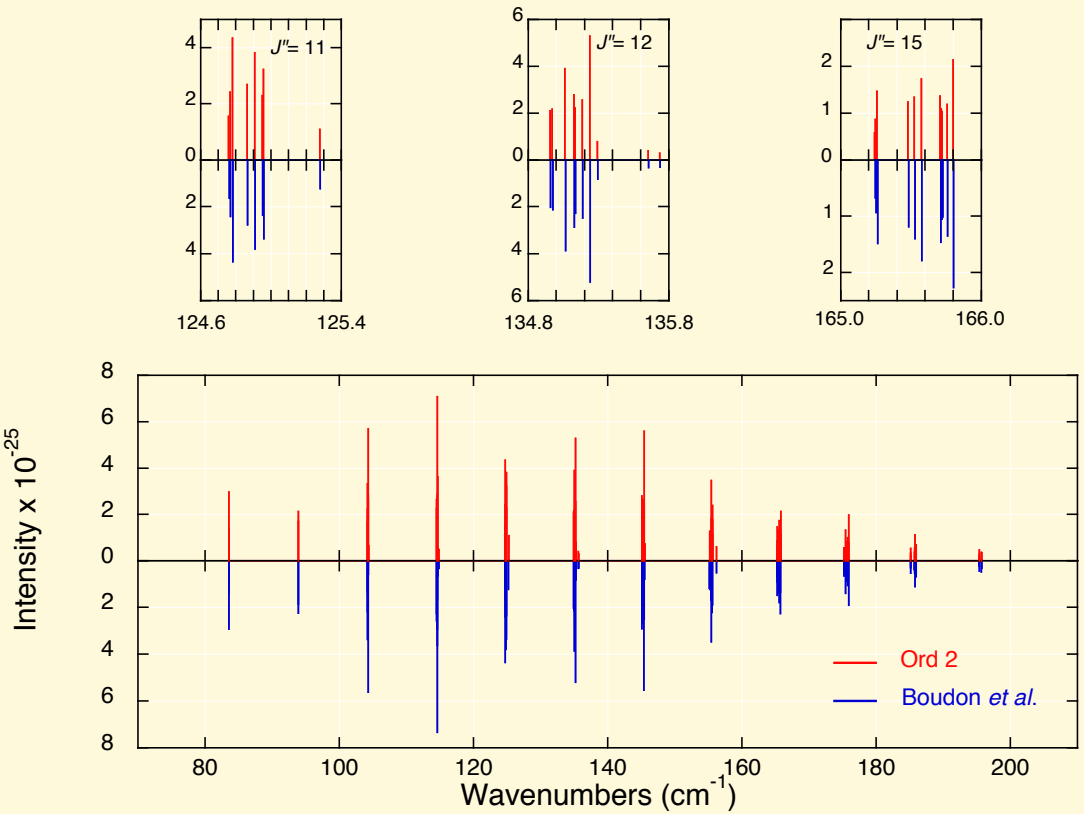
Plan

"Forbidden" spectrum of methane

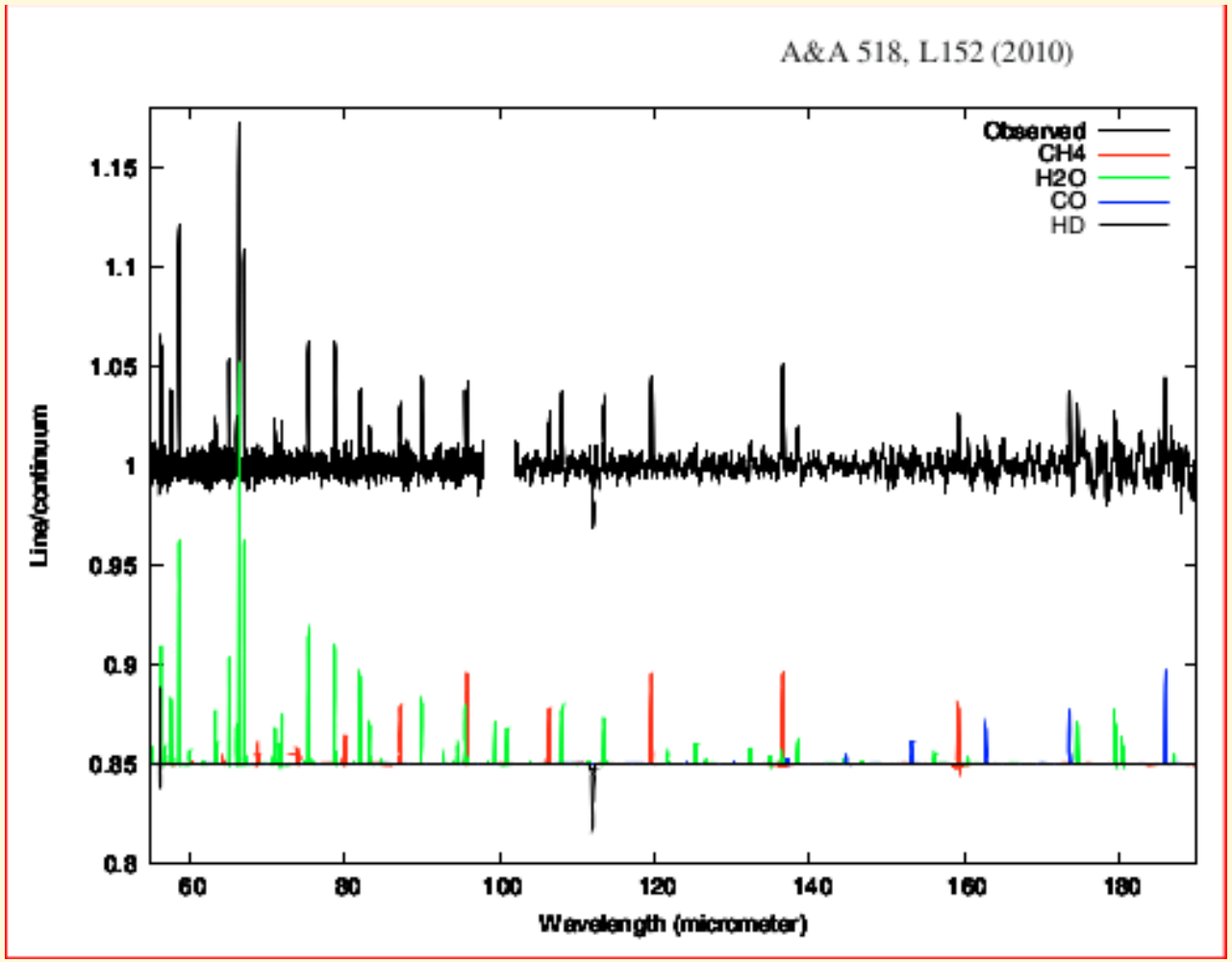
Spectre R(7-18) experimental (SOLEIL Synchrotron, V. Boudon et al.)

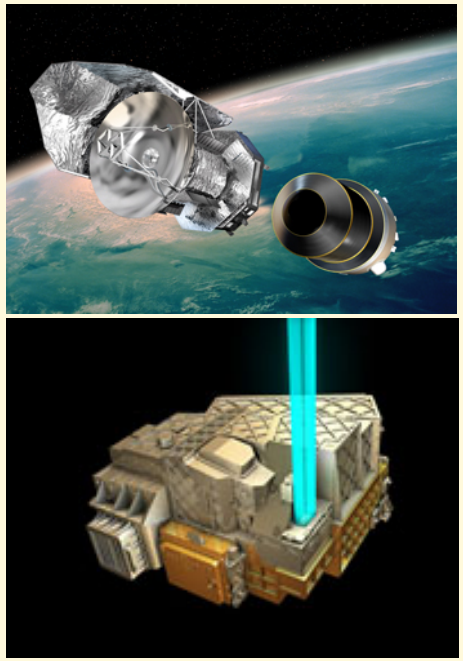
Spectre R(7-18) calculated (CONVIV code, P. Cassam-Chenaï et al.)



P. Cassam-Chenaï, J. Liévin, *The Journal of Chemical Physics* **136**, *174309*, 2012.

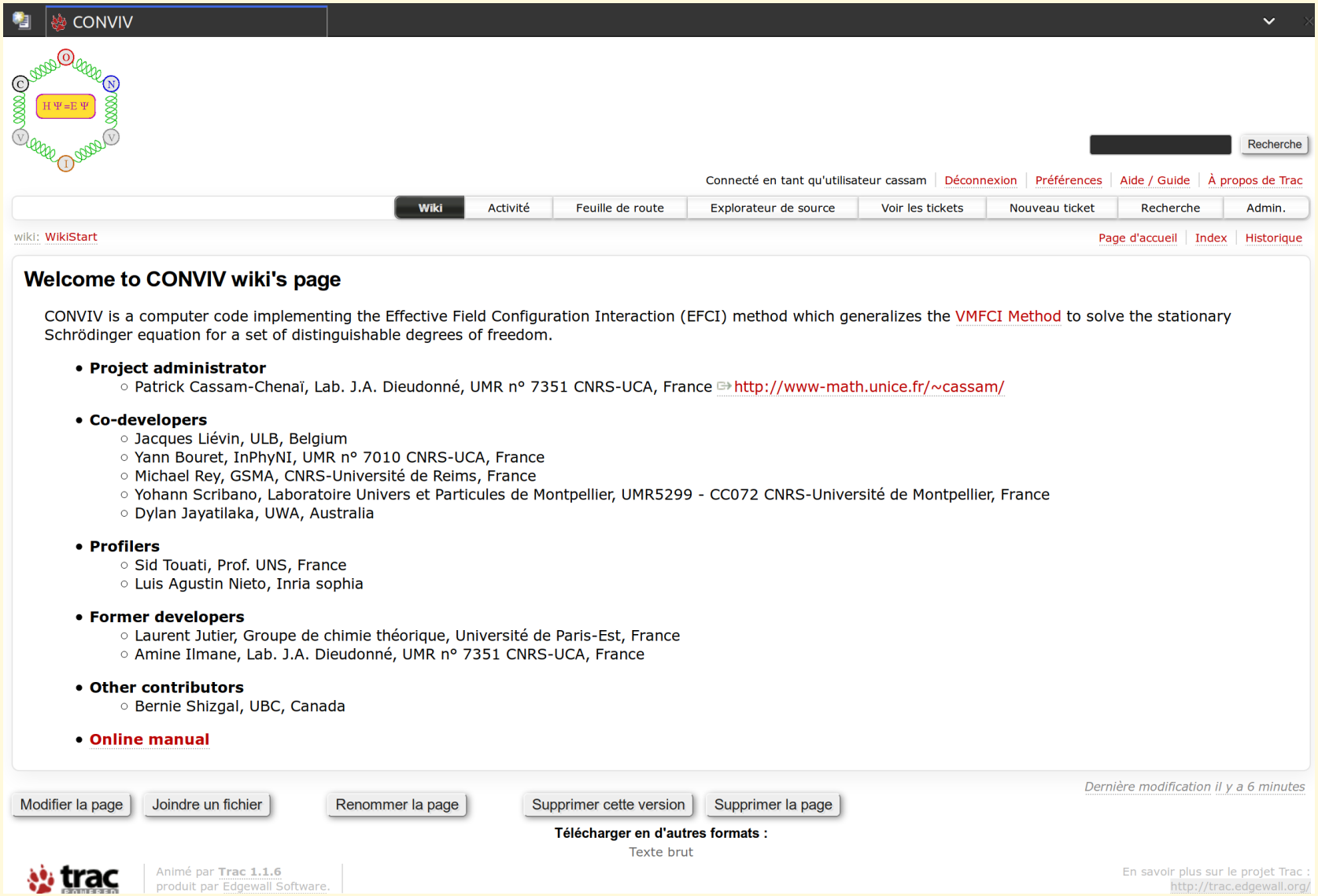
Neptune's atmosphere abundancies





(*Herschel-PACS, 2009/10/30, Lellouch et al.*)

CONVIV code


CONVIV
Recherche
Connecté en tant qu'utilisateur cassam | Déconnexion | Préférences | Aide / Guide | À propos de Trac
Wiki | Activité | Feuille de route | Explorateur de source | Voir les tickets | Nouveau ticket | Recherche | Admin.
wiki: WikiStart
Page d'accueil | Index | Historique
Welcome to CONVIV wiki's page
CONVIV is a computer code implementing the Effective Field Configuration Interaction (EFCI) method which generalizes the VMFCI Method to solve the stationary Schrödinger equation for a set of distinguishable degrees of freedom.
Project administrator
Patrick Cassam-Chenaï, Lab. J.A. Dieudonné, UMR n° 7351 CNRS-UCA, France http://www-math.unice.fr/~cassam/
Co-developers
Jacques Liévin, ULB, Belgium
Yann Bouret, InPhyNI, UMR n° 7010 CNRS-UCA, France
Michael Rey, GSMA, CNRS-Université de Reims, France
Yohann Scribano, Laboratoire Univers et Particules de Montpellier, UMR5299 - CC072 CNRS-Université de Montpellier, France
Dylan Jayatilaka, UWA, Australia
Profilers
Sid Touati, Prof. UNS, France
Luis Agustin Nieto, Inria sophia
Former developers
Laurent Jutier, Groupe de chimie théorique, Université de Paris-Est, France
Amine Ilmane, Lab. J.A. Dieudonné, UMR n° 7351 CNRS-UCA, France
Other contributors
Bernie Shizgal, UBC, Canada
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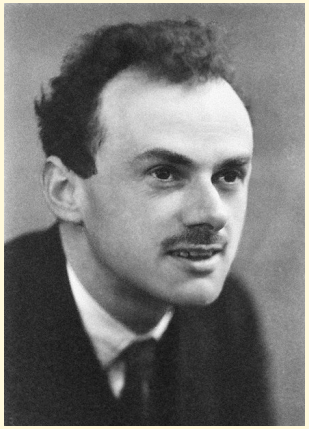
Dirac's claim (1929)



Paul Adrien Maurice Dirac
(1902 – 1984)

"the underlying physical laws necessary for the mathematical theory of ... the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble."

Schrödinger's equation

Erwin Rudolf Josef Alexander Schrödinger
(1887 – 1961)

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{x},t) = \hat{H}\Psi(\mathbf{x},t)$$

The non-relativistic Coulombian Hamiltonian

$$\hat{H}_{mol} = \hat{T}_e + \hat{T}_n + \hat{V}_{ee} + \hat{V}_{en} + \hat{V}_{nn}$$

where :

$\hat{T}_e$ (resp. $\hat{T}_n$) : Kinetic energy operator for electrons (resp. nuclei)

$\hat{V}_{ee}$ (resp. $\hat{V}_{nn}$) : Potential energy operator for electrons (resp. nuclei)

$\hat{V}_{en}$: Electron-nucleus interaction energy operator

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In general: the non-relativistic Coulombian Hamiltonian of a molecule made of N_n atoms (nuclei) of masses M_i and N_e electrons of mass m_e, which is essentially self-adjoint (T. Kato, Trans. Am. Math. Soc. **70** p.212, 1951):

$$\hat{H}_{mol} = \underbrace{\sum_{i=1}^{N_e} \frac{\hat{\mathbf{p}}_i^2}{2m_e}}_{\hat{T}_e} + \underbrace{\sum_{i=1}^{N_n} \frac{\hat{\mathbf{P}}_i^2}{2M_i}}_{\hat{T}_n} + \underbrace{\frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^{N_e} \sum_{j>i}^{N_e} \frac{1}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|}}_{\hat{V}_{ee}} - \underbrace{\frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^{N_e} \sum_{j=1}^{N_n} \frac{Z_i}{|\hat{\mathbf{r}}_i - \hat{\mathbf{R}}_j|}}_{\hat{V}_{ne}} + \underbrace{\frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^{N_n-1} \sum_{j>i}^{N_n} \frac{Z_i Z_j}{|\hat{\mathbf{R}}_i - \hat{\mathbf{R}}_j|}}_{\hat{V}_{nn}}$$

Stationary Schrödinger's equation

Case of a time independent Hamiltonian

- Look for solution of Schrödinger equation of the form $\Psi(\mathbf{x},t) = \psi(\mathbf{x})\chi(t)$:

$$\imath\hbar \frac{\partial \chi(t)}{\partial t}\psi(\mathbf{x}) = \chi(t)\hat{H}_{mol}\psi(\mathbf{x})$$

- Set $\chi(t) = Exp[-i\frac{Et}{\hbar}]$:

$$\chi(t)\left(\hat{H}_{mol} - E\right)\psi(\mathbf{x}) = 0 \; with \; \chi(t) \neq 0$$

$\Rightarrow \psi$ eigenfunction of H associated to eigenvalue E

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{x},t) = \hat{H}_{mol}\Psi(\mathbf{x},t) \quad \xrightarrow{\Psi(\mathbf{x},t)=e^{-iEt}\psi(\mathbf{x})} \quad \hat{H}_{mol}\psi(\mathbf{x}) = E\psi(\mathbf{x})$$

notation

- $\psi(\mathbf{x}) \equiv \psi(\mathbf{x}^e, \mathbf{x}^n)$ where $\mathbf{x}^e \equiv (\mathbf{r}_1, \sigma_1^e, \mathbf{r}_2, \sigma_2^e, \cdots, \mathbf{r}_{N_e}, \sigma_{N_e}^e)$ and $\mathbf{x}^n \equiv (\mathbf{R}_1, \sigma_1^n, \mathbf{R}_2, \sigma_2^n, \cdots, \mathbf{R}_{N_n}, \sigma_{N_n}^n)$

- $\hat{H}_{mol} \equiv \hat{H}_{mol}(\hat{\mathbf{r}}, \hat{\mathbf{p}}, \hat{\mathbf{R}}, \hat{\mathbf{P}})$
where $\hat{\mathbf{r}} \equiv (\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \cdots, \hat{\mathbf{r}}_{N_e})$, $\hat{\mathbf{R}} \equiv (\hat{\mathbf{R}}_1, \hat{\mathbf{R}}_2, \cdots, \hat{\mathbf{R}}_{N_n})$, with conjugate momenta $\hat{\mathbf{p}} \equiv (\hat{\mathbf{p}}_1, \hat{\mathbf{p}}_2, \cdots, \hat{\mathbf{p}}_{N_e})$, $\hat{\mathbf{P}} \equiv (\hat{\mathbf{P}}_1, \hat{\mathbf{P}}_2, \cdots, \hat{\mathbf{P}}_{N_n})$

- $\hat{H}_e(\hat{\mathbf{r}}, \hat{\mathbf{p}}) := \hat{T}_e + \hat{V}_{ee}$

- $\hat{H}_n(\hat{\mathbf{R}}, \hat{\mathbf{P}}) := \hat{T}_n + \hat{V}_{nn}$

- $\hat{V}_{en}(\hat{\mathbf{r}}, \hat{\mathbf{R}}) := \hat{V}_{en}$

Born-Oppenheimer separation

- Look for quasi-stationary states of the form:

$\psi(\mathbf{x}^e, \mathbf{x}^n) = \psi_e(\mathbf{x}^e, \mathbf{x}^n) \times \psi_n(\mathbf{x}^n)$ where $\psi_e(\mathbf{x}^e, \mathbf{x}^n)$ satisfy the

- "electronic" stationary Schrödinger equation:

$$\forall \mathbf{x}^n,\ \langle \delta_{\mathbf{x}^n} | (\hat{H}_{mol} - \hat{T}_n) \psi_e(\mathbf{x}^e, \mathbf{x}^n) \rangle = V^{bo}(\mathbf{R})\ \psi_e(\mathbf{x}^e, \mathbf{x}^n)$$

$$(\hat{H}_e(\hat{\mathbf{r}}, \hat{\mathbf{p}}) + V_{nn}(\mathbf{R}) + \hat{V}_{en}(\hat{\mathbf{r}}, \mathbf{R})) \psi_e(\mathbf{x}^e, \mathbf{x}^n) = V^{bo}(\mathbf{R})\ \psi_e(\mathbf{x}^e, \mathbf{x}^n)$$

- and the normalization condition:

$$\int d\mathbf{x}^e\ \bar{\psi}_e(\mathbf{x}^e, \mathbf{x}^n) \psi_e(\mathbf{x}^e, \mathbf{x}^n) = 1$$

Born-Oppenheimer Approximation

- Then, one is left with an effective nuclear motion stationary Schrödinger equation for $\psi_n(\mathbf{x}^n)$:

$$(\hat{T}_n + \hat{V}^{bo}(\hat{\mathbf{R}}))\ \psi_n(\mathbf{x}^n) = E_n\ \psi_n(\mathbf{x}^n)$$

- Mathematical references

* G. A. Hagedorn, A. Joye, *Comm. Math. Phys.* **223**, *583*, 2001.

"A Time-dependent Born-Oppenheimer Approximation with exponentially small error estimates"

* T. Jecko, *J. Math. Phys.* **55**, *053504*, 2014.

"On the mathematical treatment of the Born-Oppenheimer approximation"

Nuclear motions

$$\hat{H}_n(\hat{\mathbf{R}}, \hat{\mathbf{P}}) = \hat{T}_n(\hat{\mathbf{R}}, \hat{\mathbf{P}}) + \hat{V}^{bo}(\hat{\mathbf{R}})$$

$3N_n = N_{Trans} + N_{Rot} + N_{LAM} + N_{Vib}$ degrees of freedom

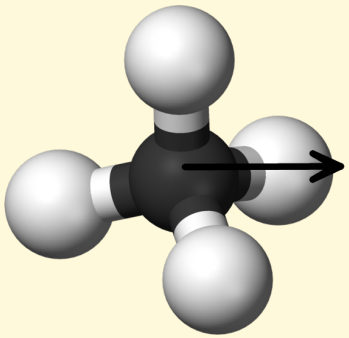
Nuclear motions

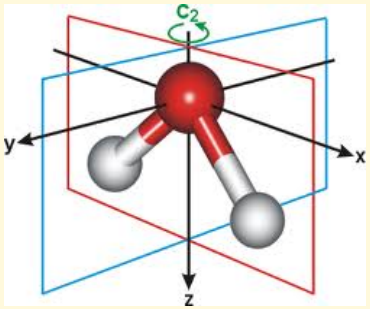
$$\hat{H}_n(\hat{\mathbf{R}}, \hat{\mathbf{P}}) = \hat{T}_n(\hat{\mathbf{R}}, \hat{\mathbf{P}}) + \hat{V}^{bo}(\hat{\mathbf{R}})$$

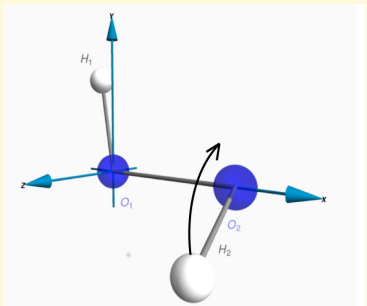
$3N_n = N_{Trans} + N_{Rot} + N_{LAM} + N_{Vib}$ degrees of freedom

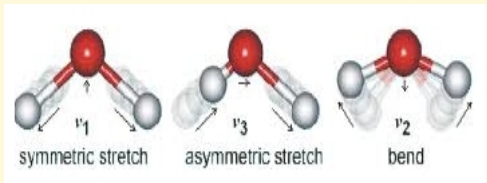
Change of coordinates

Translation	Rotation	Large Amplitude Motion	Vibrations
–	($\sim$ 1-100 cm^{-1})	($\sim$ 1-100 cm^{-1})	($\sim$ 600-4400 cm^{-1})
N_{Trans}= 3	N_{Rot}= 2 ou 3	N_{LAM}	N_{Vib}





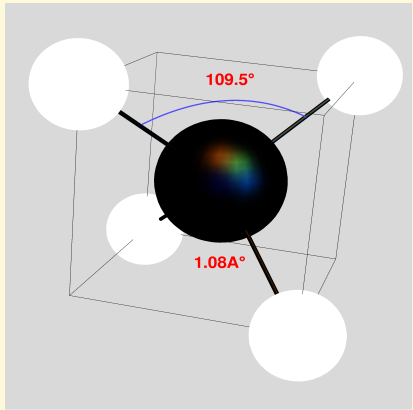




The Born-Openheimer potential is an invariant

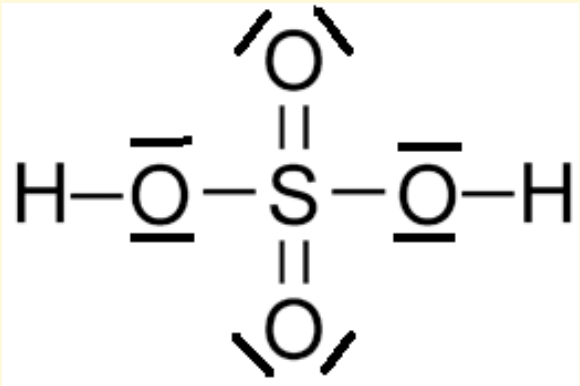
1. The BO-potential is invariant upon translation-rotations $\rightsquigarrow$ it only depends upon the internal coordinates, $\mathbf{Q}$, $V^{bo}(\mathbf{R}) = V^{bo}(\mathbf{Q})$

2. The BO-potential minima, $\mathbf{Q_0}$, correspond to equilibrium geometries of the molecule: Ex.: methane CH_4 tetrahedral equilibrium geometry:

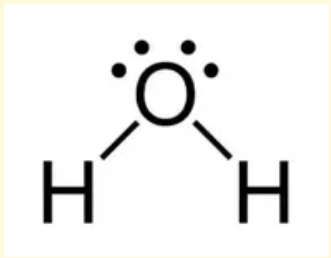


3. The BO-potential is invariant upon permutations of identical nuclei globally, and locally upon the symmetry transformations leaving an equilibrium geometry invariant $\rightsquigarrow V^{bo}(\mathbf{q} := \mathbf{Q} - \mathbf{Q_0})$.

Lewis pairs of "classical chemistry"



Sulfuric acid



Water

APG wave function

$\rightsquigarrow$ fermionic creation and annihilation operators: $a_i^\dagger, a_i$

$$[a_i, a_j]_+ = [a_i^\dagger, a_j^\dagger]_+ = 0 \ , \ [a_i, a_j^\dagger]_+ = \delta_{i,j}$$

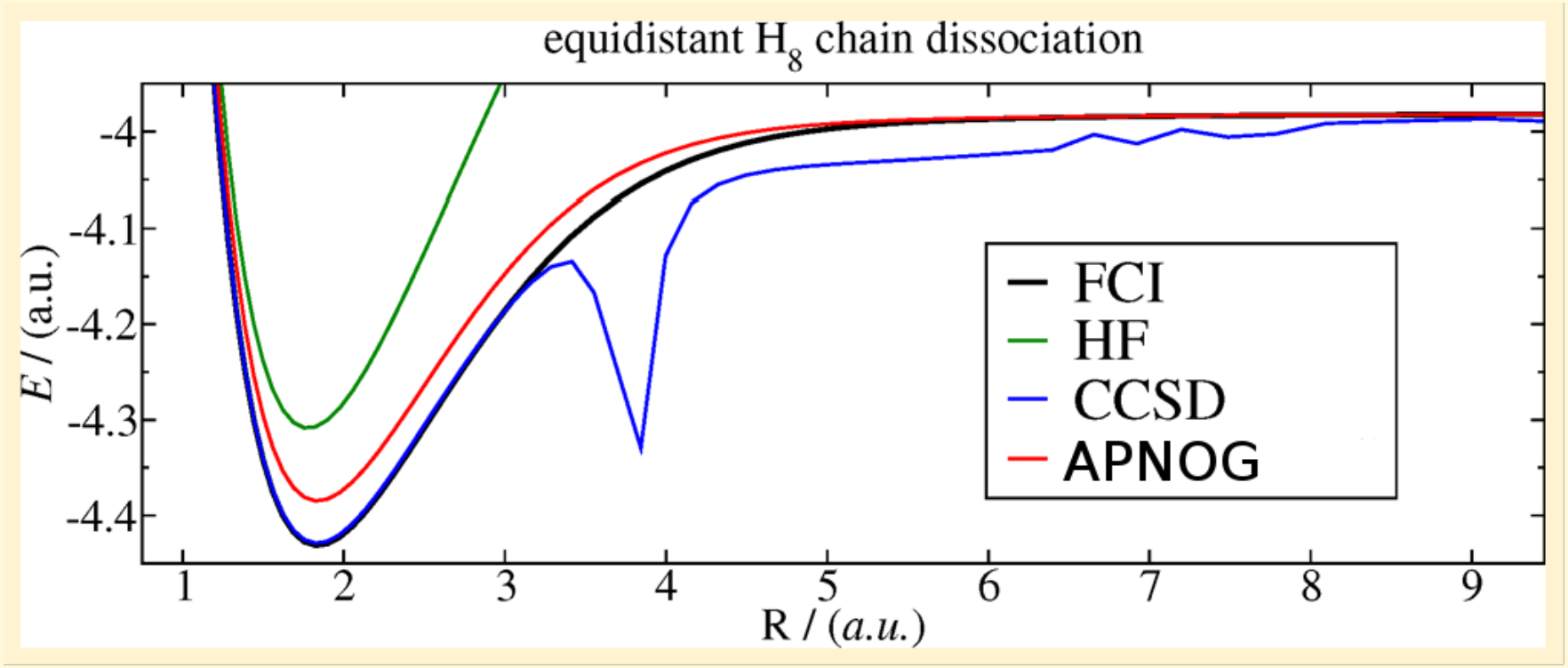
$\rightsquigarrow$ geminal: $|\Gamma\rangle = a^\dagger(\Gamma)|0\rangle$

$$a^\dagger(\Gamma) = \sum_{i_1<i_2} c_{i_1 i_2} \ a_{i_1}^\dagger a_{i_2}^\dagger$$

$\rightsquigarrow$ antisymmetrized product of geminals $\Gamma_1, \Gamma_2, \ldots, \Gamma_n$: $|\Phi_{APG}\rangle$

$$|\Phi_{APG}\rangle = a^\dagger(\Gamma_1)a^\dagger(\Gamma_2)\cdots a^\dagger(\Gamma_n)|0\rangle$$

Strongly correlated electronic systems



Limacher, Ayers, Johnson, De Baerdemacker, Van Neck, Bultinck, JCTC **9** *(2013) p.1394*

FCI: Full Configuration Interaction
HF: Hartree-Fock method
CCSD: Coupled-Cluster Single and Double
APNOG $\rightsquigarrow$ AP1roG : antisymmetrized Product of 1 reference orbital Geminals $\equiv$ pCCD

Antisymmetric Product of set-divided Geminals (APsetG)

$\rightsquigarrow$ General geminal for a 1-electron Hilbert space of finite dimension $2m$:

$$a^\dagger(\Gamma) = \sum_{1 \le i_1 < i_2 \le 2m} c_{i_1 i_2}\ a^\dagger_{i_1} a^\dagger_{i_2}$$

Each geminal is parametrized by $m(2m-1)$ independent scalars c_{i_1,i_2}

$\rightsquigarrow$ 1-electron Hilbert space partitioned into 2 subspaces of dimension m:
$\mathcal{H} = \mathcal{H}_\alpha \oplus \mathcal{H}_\beta, \qquad dim\mathcal{H}_\alpha = dim\mathcal{H}_\beta = m, \qquad \mathcal{H}_\alpha \leftrightarrow a^\dagger, \mathcal{H}_\beta \leftrightarrow \bar{a}^\dagger$

$\rightsquigarrow$ APsetG geminal: $|\Gamma_{\text{set}}\rangle = a^\dagger(\Gamma_{\text{set}})|0\rangle$ $\qquad \hat{S}_z$ eigenfunctions

$$a^\dagger(\Gamma_{\text{set}}) = \sum_{1 \le i_1, i_2 \le m} c_{i_1 i_2}\ a^\dagger_{i_1} \bar{a}^\dagger_{i_2} \qquad S_z = 0$$

Each APsetG geminal is parametrized by m^2 independent scalars c_{i_1,i_2}

Antisymmetric Product of set-divided Geminals (APsetG)

$\rightsquigarrow$ APsetG geminal: $|\Gamma_{\text{set}}\rangle = a^\dagger(\Gamma_{\text{set}})|0\rangle$

$$a^\dagger(\Gamma_{\text{set}}) = \sum_{1\leq i_1,i_2\leq m} c_{i_1 i_2}\ a^\dagger_{i_1}\bar{a}^\dagger_{i_2}$$

Γ_{set} is parametrized by an $m \times m$ matrix: $C = (c_{i_1,i_2})$

$\rightsquigarrow$ $\hat{S}^2$-Spin-adapted geminals

Singlet $\Rightarrow c_{i_1 i_2} = c_{i_2 i_1}$ i.e. C symmetric

$$a^\dagger(\Gamma_{\text{set}}) = \sum_{1\leq i_1\leq m} c_{i_1 i_1}\ a^\dagger_{i_1}\bar{a}^\dagger_{i_1} + \sum_{1\leq i_1<i_2\leq m} c_{i_1 i_2}\ \left(a^\dagger_{i_1}\bar{a}^\dagger_{i_2} + a^\dagger_{i_2}\bar{a}^\dagger_{i_1}\right)$$

Triplet $\Rightarrow c_{i_1 i_2} = -c_{i_2 i_1}$ i.e. C antisymmetric

$$a^\dagger(\Gamma_{\text{set}}) = \sum_{1\leq i_1<i_2\leq m} c_{i_1 i_2}\ \left(a^\dagger_{i_1}\bar{a}^\dagger_{i_2} - a^\dagger_{i_2}\bar{a}^\dagger_{i_1}\right)$$

APsetG overlap formula

* General overlap closed formula: $\Gamma_i \leftrightarrow C_i$, $\Gamma'_j \leftrightarrow C'_j$

$$\langle \Gamma_1 \wedge \cdots \wedge \Gamma_k | \Gamma'_1 \wedge \cdots \wedge \Gamma'_k \rangle = \langle 0 | a(\Gamma_k) \cdots a(\Gamma_2) a(\Gamma_1) a^\dagger(\Gamma'_1) a^\dagger(\Gamma'_2) \cdots a^\dagger(\Gamma'_k) | 0 \rangle =$$

$$\sum_{\substack{0 \le N_{k,0}, \ldots, N_{k,k} \le k \\ \sum_{i=0}^{k} N_{k,i} = \sum_{i=0}^{k} i N_{k,i} = k}} (-1)^{N_{k,0}} \sum_{\sigma, \sigma' \in \mathfrak{S}_k} \prod_{i=1}^{k} \frac{\prod_{j=1}^{N_{k,i}} tr\left[C^\dagger_{\sigma\left(\sum_{p=0}^{i-1} p N_{k,p} + (j-1)i+1\right)} C'_{\sigma'\left(\sum_{p=0}^{i-1} p N_{k,p} + (j-1)i+1\right)} \cdots C^\dagger_{\sigma\left(\sum_{p=0}^{i-1} p N_{k,p} + ji\right)} C'_{\sigma'\left(\sum_{p=0}^{i-1} p N_{k,p} + ji\right)} \right]}{i^{N_{k,i}} \, N_{k,i}!},$$

* Ex.: $k = 3 \rightsquigarrow$ 3 partitions of k

- $N_{3,1} = 3,\ N_{3,2} = 0,\ N_{3,3} = 0 \quad \rightsquigarrow \quad 3 * 1 + 0 * 2 + 0 * 3 = 3 = 1 + 1 + 1, \quad N_{3,0} = 0$

$$\sum_{\sigma, \sigma' \in \mathfrak{S}_3} \frac{tr\left[C^\dagger_{\sigma(1)} C'_{\sigma'(1)}\right] \, tr\left[C^\dagger_{\sigma(2)} C'_{\sigma'(2)}\right] \, tr\left[C^\dagger_{\sigma(3)} C'_{\sigma'(3)}\right]}{3!}$$

- $N_{3,1} = 1,\ N_{3,2} = 1,\ N_{3,3} = 0 \quad \rightsquigarrow \quad 1 * 1 + 1 * 2 + 0 * 3 = 3 = 0 + 1 + 2, \quad N_{3,0} = 1$

$$- \sum_{\sigma, \sigma' \in \mathfrak{S}_3} \frac{tr\left[C^\dagger_{\sigma(1)} C'_{\sigma'(1)}\right] \, tr\left[C^\dagger_{\sigma(2)} C'_{\sigma'(2)} C^\dagger_{\sigma(3)} C'_{\sigma'(3)}\right]}{2}$$

- $N_{3,1} = 0,\ N_{3,2} = 0,\ N_{3,3} = 1 \quad \rightsquigarrow \quad 0 * 1 + 0 * 2 + 1 * 3 = 3 = 0 + 0 + 3, \quad N_{3,0} = 2$

$$\sum_{\sigma, \sigma' \in \mathfrak{S}_3} \frac{tr\left[C^\dagger_{\sigma(1)} C'_{\sigma'(1)} C^\dagger_{\sigma(2)} C'_{\sigma'(2)} C^\dagger_{\sigma(3)} C'_{\sigma'(3)}\right]}{3}$$

APsetG overlap formula

$$\langle \Phi_{APG} | \Phi'_{APG} \rangle = \langle 0 | a(\Gamma_k) \cdots a(\Gamma_2) a(\Gamma_1) a^\dagger(\Gamma'_1) a^\dagger(\Gamma'_2) \cdots a^\dagger(\Gamma'_k) | 0 \rangle$$

Scaling of the general overlap formula $\rightsquigarrow$ Exponential computational cost

$$\sum_{\substack{0 \leq N_{k,0}, \ldots, N_{k,k} \leq k \\ \sum_{i=0}^{k} N_{k,i} = \sum_{i=0}^{k} i N_{k,i} = k}} \quad \underset{k \to +\infty}{\overset{nb.\ of\ terms}{\longrightarrow}} \quad \frac{1}{4k\sqrt{3}} \exp\left(\pi \sqrt{\frac{2k}{3}}\right)$$

Antisymmetrized Product of Interacting Geminals

APIG All C_i, C'_i matrices are diagonal

$$\forall i,\ C_i = \begin{pmatrix} \lambda_1^i & 0 & \dots & 0 \\ 0 & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & 0 \\ 0 & \dots & 0 & \lambda_m^i \end{pmatrix},\ C'_i = \begin{pmatrix} \lambda'^i_1 & 0 & \dots & 0 \\ 0 & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & 0 \\ 0 & \dots & 0 & \lambda'^i_m \end{pmatrix}$$

- Seniority-0 geminals $\quad a^\dagger(\Gamma_{\text{set}}) = \sum_{1\le j\le m} \lambda_j^i\ a_j^\dagger \bar{a}_j^\dagger$
- $tr\left[C_{a_1}^\dagger C'_{b_1} \cdots\ C_{a_i}^\dagger C'_{b_i}\right] \to \sum_{j=1}^{m} \lambda_j^{a_1} \cdots \lambda_j^{a_i} \lambda'^{b_1}_j \cdots \lambda'^{b_i}_j$
- Scaling still $\frac{1}{4k\sqrt{3}} \exp\left(\pi\sqrt{\frac{2k}{3}}\right) \rightsquigarrow$ AP1roG, Richardson-Gaudin states

Antisymmetrized Geminal Power (AGP)

aka Projected Bardeen-Cooper-Schrieffer wave function $\forall i, C_i = C_0$

- $\sum_{\sigma,\sigma' \in \mathfrak{S}_k} \to (k!)^2$
- $tr\Big[C^\dagger_{\sigma(\sum_{p=0}^{i-1} pN_{k,p}+(j-1)i+1)} C_{\sigma'(\sum_{p=0}^{i-1} pN_{k,p}+(j-1)i+1)} \cdots C^\dagger_{\sigma(\sum_{p=0}^{i-1} pN_{k,p}+ji)} C_{\sigma'(\sum_{p=0}^{i-1} pN_{k,p}+ji)}\Big]$

$$\to tr[(C_0^\dagger C_0)^i]$$

$\rightsquigarrow$ Without loss of generality: $\forall i,j, \quad (C_0)_{i,j} = \delta_{i,j}\eta_i$

- $$tr[(C_0^\dagger C_0)^i] = \sum_{j=1}^{m} (\eta_j^2)^i$$
- $$\langle 0|a(\Gamma_0)^k a^\dagger(\Gamma_0)^k|0\rangle = (k!)^2 \times \Big(\sum_{1\le i_1<\ldots<i_k\le m} \eta_{i_1}^2 \cdots \eta_{i_k}^2 \Big)$$
- Ex. $k=3$, $$\Big(\frac{\sum_{i=1}^{m} \eta_i^6}{3} - \frac{\sum_{i=1}^{m} \eta_i^2 \times \sum_{j=1}^{m} \eta_j^4}{2} + \frac{\sum_{i=1}^{m} \eta_i^2 \times \sum_{j=1}^{m} \eta_j^2 \times \sum_{k=1}^{m} \eta_k^2}{6} \Big)$$

Antisymmetrized Product of Strongly-orthogonal Geminals

APSG aka 1-orthogonal geminals wave function

$$\forall i,j \; i \neq j, \; C_i C_j = 0$$

- Only the partition $k = 1 + 1 + \cdots + 1$ contributes
- $\sum_{\sigma,\sigma' \in \mathfrak{S}_k} \frac{tr\left[C^\dagger_{\sigma(1)} C'_{\sigma'(1)}\right] \; \cdots \; tr\left[C^\dagger_{\sigma(k)} C'_{\sigma'(k)}\right]}{k!} \to \sum_{\sigma \in \mathfrak{S}_k} \to k!$
- $\langle 0 | a(\Gamma_k) \cdots a(\Gamma_2) a(\Gamma_1) a^\dagger(\Gamma'_1) a^\dagger(\Gamma'_2) \cdots a^\dagger(\Gamma'_k) | 0 \rangle = tr\left[C^\dagger_1 C'_1\right] \; \cdots \; tr\left[C^\dagger_k C'_k\right]$

Antisymmetrized Product of Strongly-orthogonal Geminals

More explicitly

$$C_i = \begin{pmatrix} 0 & \cdots & 0 & \cdots & \cdots & \cdots & 0 & \cdots & 0 \\ \vdots & \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & \cdots & 0 & \cdots & \cdots & \cdots & 0 & \cdots & 0 \\ 0 & \cdots & 0 & \lambda_1^i & \cdots & 0 & 0 & \cdots & 0 \\ 0 & \cdots & 0 & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ 0 & \cdots & 0 & 0 & \cdots & \lambda_{d_i}^i & 0 & \cdots & 0 \\ 0 & \cdots & 0 & \cdots & \cdots & \cdots & 0 & \cdots & 0 \\ \vdots & \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & \cdots & 0 & \cdots & \cdots & \cdots & 0 & \cdots & 0 \end{pmatrix}$$

- Restricted Hartree-Fock: $\forall i, \quad d_i = 1$

Strong orthogonality shortcomings

Ground state energies in Hartree at "experimental" geometry (STO-3G calculations)

System	LiH	Be	Li_2	BeH_2	BH	Be_2
E^0_{FCI}	-7.882392	-14.403655	-14.667340	-15.594861	-24.809945	-28.804345
E^0_{GSCF}	-7.882372	-14.403655	-14.667114	-15.594715	-24.809938	-28.803212
with 2-orthogonality	-7.882368	-14.403654	-14.667090	-15.594703	-24.809920	-28.803080
APSG	-7.882203	-14.403630	-14.666584	-15.588630	-24.807908	-28.781789
E^0_{RHF}	-7.862002	-14.351880	-14.638725	-15.559405	-24.752780	-28.698990

Electric dipole moments

System	LiH	BH
D^z_{FCI}	-4.6201	0.6138
D^z_{GSCF}	-4.6197	0.6138
with 2-orthogonality	-4.6189	0.6142
D^z_{APSG}	-4.6269	0.6861
D^z_{RHF}	-4.8578	0.9569

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