

Pre-Born–Oppenheimer Molecular Structure Theory

Edit Mátyus

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Quantum chemistry and quantum mechanics

Born–Oppenheimer separation

Electronic structure theory

- In the external electric field of the atomic nuclei
- Kinetic energy operator:

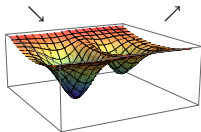
$$-\sum_{i=1}^{n_e} \frac{1}{2m_e} \Delta_{r_i}$$

- Potential energy:

$$\sum_{i=1}^{n_e} \sum_{j>i}^{n_e} \frac{1}{r_{ij}} - \sum_{i=1}^{n_e} \sum_{n=1}^{n_n} \frac{Z_n}{r_{in}}$$

Nuclear motion theory

- Translational and rotational invariance for an isolated molecule
- Kinetic energy operator: curvilinear coordinates, $\hat{T}(\rho)$
- Potential energy: $(3n_n - 6)$ -dimensional representations



potential energy surface (PES)

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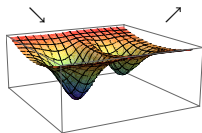
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The tremendous success of the usual practice might perhaps be best regarded as a tribute to the insight and ingenuity of the practitioners for inventing an effective variant of quantum theory for chemistry.

B. T. Sutcliffe and R. G. Woolley, J. Chem. Phys. 137, 22A544 (2012).

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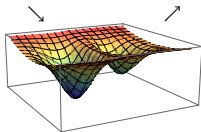
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Few-particle quantum theory

Electrons & atomic nuclei

- Translational and rotational invariance for an isolated molecule

- Kinetic energy operator:

$$-\sum_{i=1}^{n_p+1} \frac{1}{2m_i} \Delta_{r_i} \text{ or } \hat{T}(\rho)$$

- Potential energy:

$$\sum_{i=1}^{n_p+1} \sum_{j>i}^{n_p+1} \frac{q_i q_j}{r_{ij}}$$

Molecules as few-particle quantum systems

Very accurate numerical results

- **numerical solution of three-particle systems**
Bishop and co-workers, Frolov and co-workers, ...
- **positronium-electron complexes and nuclear physics**
Suzuki and Varga, ...
- **high-accuracy calculations for molecules**
Adamowicz and co-workers, ...

⇒ high-resolution spectroscopy (incl. rel. effects)

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Interesting conceptual questions

- **The molecular structure conundrum**
Weininger, J. Chem. Educ. 61, 939 (1984).
Woolley, Sutcliffe, Primas, Claverie and Diner, ..., Isr. J. Chem. vol. 19 (1980)
- **a single $\langle r_{C-H} \rangle$ in an organic molecule**
e.g., B. T. Sutcliffe and R. G. Woolley, Chem. Phys. Lett. 408, 445 (2005).
- **linear or triangular H_3^+ ?**
M. Cafiero and L. Adamowicz, Chem. Phys. Lett., 387, 136 (2004).
 $\langle \alpha_{HHH} \rangle = (0^\circ + 180^\circ + 0^\circ)/3 = 60^\circ$ or $\langle \alpha_{HHH} \rangle = (60^\circ + 60^\circ + 60^\circ)/3 = 60^\circ$

⇒ classical features in a quantum description

Molecules as few-particle quantum systems

⇒ *pre*-Born–Oppenheimer theory

Schrödinger equation

$$\hat{H}\Psi = E\Psi \quad \text{with} \quad \hat{H}(\mathbf{m}, \mathbf{q}; \mathbf{r}) = - \sum_{i=1}^{n_p+1} \frac{1}{2m_i} \Delta_{r_i} + \sum_{i=1}^{n_p+1} \sum_{j>i}^{n_p+1} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (1)$$

⇒ mass and electric charge: m_i, q_i ($i = 1, 2, \dots, n_p + 1$) parameters

Pauli principle

Spin statistics for fermions and bosons

⇒ spin: s_i ($i = 1, 2, \dots, n_p + 1$) parameters

$3(n_p + 1)$ physical parameters: m_i, q_i, s_i ($i = 1, 2, \dots, n_p + 1$)

⇒ Variational solution with explicitly correlated Gaussians (ECGs)

Adamowicz and co-workers, Suzuki and Varga

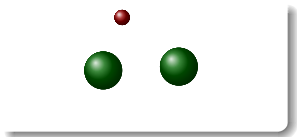
Pre-Born–Oppenheimer molecular structure theory

- **Molecular structure in quantum mechanics**
- Non-relativistic limit for small molecules

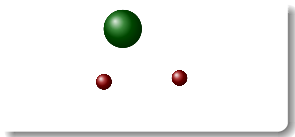
On the Born–Oppenheimer approximation

We describe the six degrees of freedom of the ground state of the **helium atom** (considered as 3-particle problem with the center-of-mass motion separated) as a problem of two interacting particles in an external Coulomb potential. However, in the case of the molecule H_2^+ we **discuss the very same type of differential equation in an entirely different way**, and split the 6 degrees of freedom into 1 vibrational mode, 2 rotational modes, and 3 electronic type degrees of freedom. This qualitatively different description does by no means follow from a purely mathematical discussion.

HANS PRIMAS: Chemistry, Quantum Mechanics and Reductionism
(Springer-Verlag, Berlin, Heidelberg and New York, 1981)



vs.



Molecular structure in quantum mechanics

Quantum chemistry: quantum mechanics + Born–Oppenheimer approximation

- equilibrium structure: local minimum structure of the PES
- we put in the molecular structure into this theoretical description

Molecular structure in quantum mechanics

Quantum chemistry: quantum mechanics + Born–Oppenheimer approximation

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Quantum theory and chemistry?

How to recover the classical molecular structure from a purely quantum mechanical description?

- a non-trivial problem: “The molecular structure conundrum”
Weininger, J. Chem. Educ. 61, 939 (1984);
Woolley, Sutcliffe, Primas, Claverie and Diner, ..., Isr. J. Chem. vol. 19 (1980)

Let's calculate expectation values for the molecular structural parameters with the system's wave function...

- **there is only a single $\langle r_{C-H} \rangle$ for any organic molecule**
e.g., B. T. Sutcliffe and R. G. Woolley, Chem. Phys. Lett. 408, 445 (2005).
- given that $\langle \alpha_{HHH} \rangle = 60^\circ$ for the ground state wave function of H_3^+ ,
can we decide whether it is **linear or triangular** (or both or something else)?
M. Cafiero and L. Adamowicz, Chem. Phys. Lett., 387, 136 (2004).
 $\langle \alpha_{HHH} \rangle = (0^\circ + 180^\circ + 0^\circ)/3 = 60^\circ$ or $\langle \alpha_{HHH} \rangle = (60^\circ + 60^\circ + 60^\circ)/3 = 60^\circ$

⇒ problem: quantum mechanical indistinguishability of identical particles

Probabilistic interpretation of the wave function

Structural parameters

do not have sharp, dispersionless values, but they are characterized by **some probability density function**

1-particle density

$$\rho_{P,a}(\mathbf{R}_1) = \langle \Psi(\mathbf{r}) | \delta(\mathbf{r}_a - \mathbf{r}_P - \mathbf{R}_1) | \Psi(\mathbf{r}) \rangle \quad (2)$$

2-particle density

$$D_{P,ab}^{(2)}(\mathbf{R}_1, \mathbf{R}_2) = \langle \Psi(\mathbf{r}) | \delta(\mathbf{r}_a - \mathbf{r}_P - \mathbf{R}_1) \delta(\mathbf{r}_b - \mathbf{r}_P - \mathbf{R}_2) | \Psi(\mathbf{r}) \rangle \quad (3)$$

$$\Gamma_{P,ab}(\alpha) = \int_0^\infty dR_1 R_1^2 \int_0^\infty dR_2 R_2^2 D_{P,ab}^{(2)}(\mathbf{R}_1, \mathbf{R}_2) \quad \text{with} \quad \mathbf{R}_1^\top \mathbf{R}_2 = R_1 R_2 \cos \alpha \quad (4)$$

On the emergence of molecular structure...

Coulomb Hamiltonian for $\{a^\pm, a^\pm, b^\mp\}$ systems

$$\hat{H}(m_a, m_b; \mathbf{r}) = -\frac{1}{2m_a}\Delta_{r_1} - \frac{1}{2m_a}\Delta_{r_2} - \frac{1}{2m_b}\Delta_{r_3} + \frac{1}{r_{12}} - \frac{1}{r_{13}} - \frac{1}{r_{23}} \quad (5)$$

- charge-inversion symmetry
- mass-scale similarity

$$\hat{H}(\eta m_a, \eta m_b; \mathbf{r}) = \eta \hat{H}(m_a, m_b, \eta \mathbf{r}), \quad \eta \in \mathbb{R} \setminus \{0\} \quad (6)$$

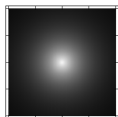
- bound for all m_a/m_b values [Martin et al., Phys. Rev. A 46, 3697 (1992)]
- let us consider the transition: $\text{H}^- \rightarrow \text{H}_2^+$

Particle density vs. mass ratio

$\rho_{0,a}(X, Y, 0)$ vs. m_a/m_b for $\{a^\pm, a^\pm, b^\mp\}$ -type systems

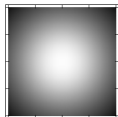
$N = 0, p = +1$ (COM is at the middle of each plot)

$\frac{m_a}{m_b}$: 0.000543

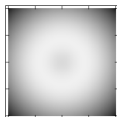


H⁻
{e⁻, e⁻, p⁺}

0.5

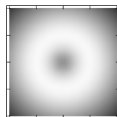


1

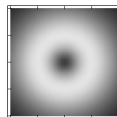


Ps⁻
{e⁻, e⁻, e⁺}

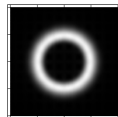
2



5



1840



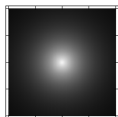
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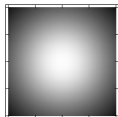
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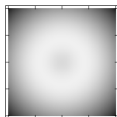


H^-
 $\{e^-, e^-, p^+\}$

0.5

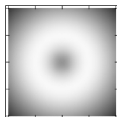


1

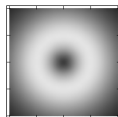


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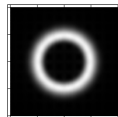
2



5



1840



H_2^+
 $\{p^+, p^+, e^-\}$

Superposition vs. rotating dumbbell

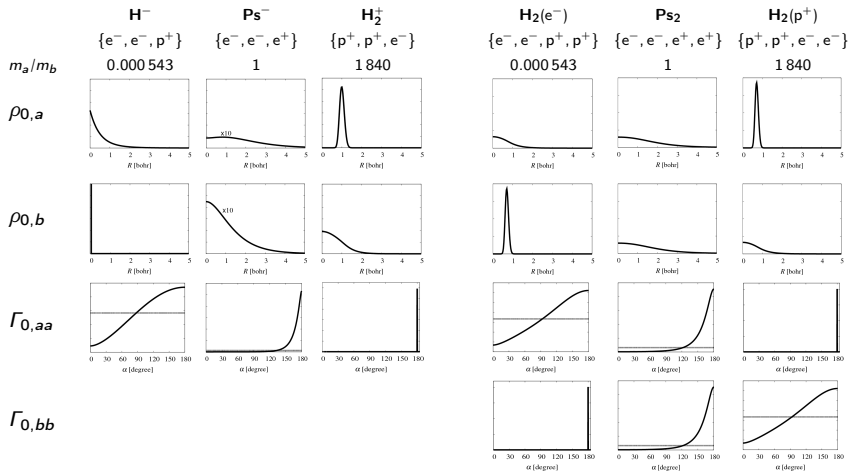


or



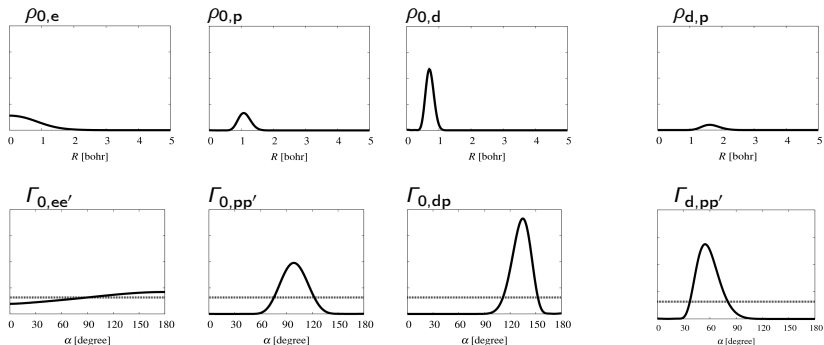
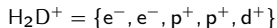
Radial and angular densities

$\{a^\pm, a^\pm, b^\mp\}$ - and $\{a^\pm, a^\pm, b^\mp, b^\mp\}$ -type systems



⇒ “mass-polarization effects” [Fröman & Kinsey (1961) and Woolley (1976)]

Radial and angular densities



Remark: qualitative features of the radial and angular densities converged quickly

⇒ **“molecular structure seen as correlation effects for the nuclei”**

Claverie and Diner, *Isr. J. Chem.* 19, 54 (1980).

⇒ N.B. “traditional route”: introduce internal coordinates to describe nuclear motion...

Pre-Born–Oppenheimer molecular structure theory

- Molecular structure in quantum mechanics
- **Non-relativistic limit for small molecules**

Molecules as few-particle quantum systems

⇒ *pre*-Born–Oppenheimer theory

Schrödinger equation

$$\hat{H}\Psi = E\Psi \quad \text{with} \quad \hat{H}(\mathbf{m}, \mathbf{q}; \mathbf{r}) = - \sum_{i=1}^{n_p+1} \frac{1}{2m_i} \Delta_{\mathbf{r}_i} + \sum_{i=1}^{n_p+1} \sum_{j>i}^{n_p+1} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (7)$$

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Pauli principle

Spin statistics for fermions and bosons

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⇒ **Variational solution with explicitly correlated Gaussians (ECGs)**

Adamowicz and co-workers, Suzuki and Varga

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⇒ Variational solution with explicitly correlated Gaussians (ECGs)

Adamowicz and co-workers, Suzuki and Varga

⇒ Challenge: molecules with various quantum numbers

Variational solution with explicitly correlated Gaussian functions

Key ingredients of the variational procedure

Input: number of particles, mass, electric charge, spin

Quantum numbers: total angular momentum (N, M_N), parity (p), spin ($S_a, M_{S_a}; S_b, M_{S_b}; \dots$)

- **Cartesian coordinates**
laboratory-fixed or translationally invariant (linear transformation)
- **Hamiltonian is simple** in Cartesian coordinates
- **symmetry-adapted explicitly correlated Gaussian functions**
 - global vector representation
a generalized angular momentum coupling scheme for a variational approach
[Y. Suzuki, J. Usukura, and K. Varga, J. Phys. B 31, 31 (1998)]
 - flexible parameterization
- **analytic matrix elements**
- **generalized eigenvalue problem, direct solution**
($\sim 1000 \times 1000$ real symmetric matrices)
- ◇ **variational principle**
optimization of the basis function parameters (stochastic and Powell's method)

Variational solution with explicitly correlated Gaussian functions

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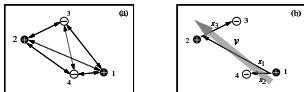
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Symmetry-adapted basis functions

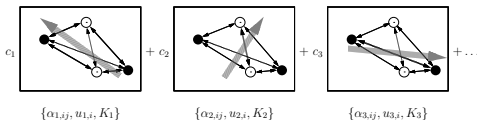
Basis function



$$\phi^{(\lambda)}(\mathbf{r}; \mathbf{A}, \mathbf{u}, K) = |\mathbf{v}|^{2K+N} Y_N^{MN}(\hat{\mathbf{v}}) \exp\left(-\frac{1}{2} \sum_{i=1}^{n_p+1} \sum_{j>i}^{n_p+1} \alpha_{ij} (\mathbf{r}_i - \mathbf{r}_j)^2\right) \quad \text{with} \quad \mathbf{v} = \sum_{i=1}^{n_p+1} u_i \mathbf{r}_i$$

parameters: $\alpha_{ij}(\mathbf{A}), u_i(\mathbf{u}), K$ $[\lambda = (N, p), p = (-1)^N]$

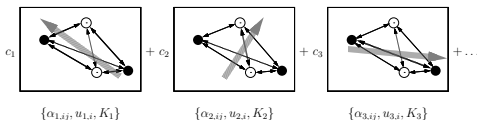
Basis-set expansion



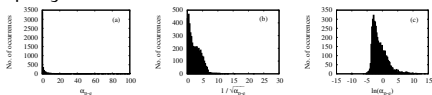
$$\Psi_0^{(\lambda, \zeta)} = c_1 \hat{\mathcal{A}}\{\chi_1^{(\zeta)} \phi^{(\lambda)}(\mathbf{r}; \{\alpha_{ij,1}, u_{i,1}, K_1\})\} + c_2 \hat{\mathcal{A}}\{\chi_2^{(\zeta)} \phi^{(\lambda)}(\mathbf{r}; \{\alpha_{ij,2}, u_{i,2}, K_2\})\} + c_3 \hat{\mathcal{A}}\{\chi_3^{(\zeta)} \phi^{(\lambda)}(\mathbf{r}; \{\alpha_{ij,3}, u_{i,3}, K_3\})\} + \dots$$

parameter set: $\{\alpha_{l,ij}(\mathbf{A}_l), u_{l,i}(\mathbf{u}_l), K_l, (l = 1, \dots, N_b)\}$

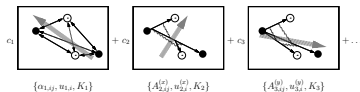
Parameterization of the basis functions



- variational principle
- fast eigenvalue estimator for a rank-1 update (known theorem)
- sampling-importance sampling



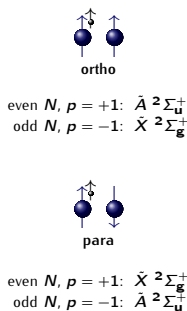
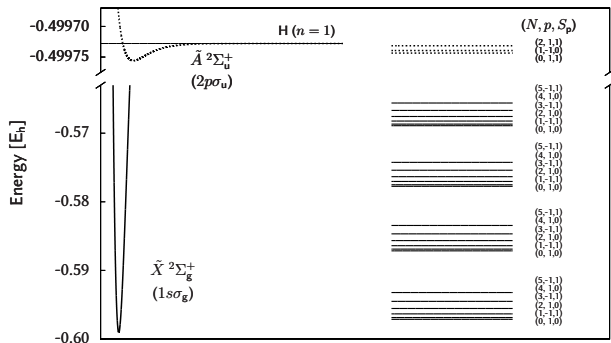
- fine-tuning: random walk or Powell's method
- multi-channel optimization



- parameter-transfer approach

$$\psi(A') = \sum_{l=1}^{N_b} c_l \phi_l^{(A')}[\mathcal{P}_l(A)]$$

Test case: $H_2^+ = \{p^+, p^+, e^-\}$



Energy levels and dissociation energies (examples)

N	p	S_p	E / E_h	D / cm^{-1}	Assignment
2	1	1	-0.499 731 516(7)	0.807(1)	$\tilde{A} \ 2\Sigma_u^+, \nu = 0$; ortho
...					
0	1	0	-0.597 139 060(4)	21 379.290(2)	$\tilde{X} \ 2\Sigma_{g+}^+, \nu = 0$; para



parameterization:

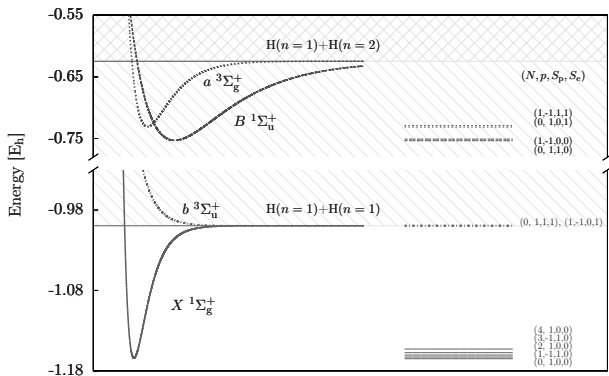
- sampling-importance sampling and Powell's method for fine-tuning
- parameter-transfer approach

Calculated energy levels of H_2 with $N = 0, 1, \text{ and } 2$
total (orbital plus rotational) angular momentum quantum number

$(N, p, S_p, S_e)^a$	E/E_h^b	$\Delta E_{\text{Ref}}/\mu E_h^c$	Ref.	Assignment ^d
(0, +1, 0, 0)	-1.164 025 030	-0.000 6	[1]	$X^1\Sigma_g^+$
(1, -1, 1, 0)	-1.163 485 171	-0.001 4	[1]	$X^1\Sigma_g^+$
(2, +1, 0, 0)	-1.162 410 408	-0.001 9	[1]	$X^1\Sigma_g^+$
(0, +1, 1, 0)	-0.753 027 186	0.135 4	[2]	$B^1\Sigma_u^+$
(1, -1, 0, 0)	-0.752 850 233	0.834 2	[2]	$B^1\Sigma_u^+$
(2, +1, 1, 0)	-0.752 498 022	0.918 8	[2]	$B^1\Sigma_u^+$
(0, +1, 0, 1)	-0.730 825 193	-0.006 9	[3]	$a^3\Sigma_g^+$
(1, -1, 1, 1)	-0.730 521 418	0.008 0	[3]	$a^3\Sigma_g^+$
(2, +1, 0, 1)	-0.729 916 268	0.047 9	[3]	$a^3\Sigma_g^+$
(0, +1, 1, 1)	[-0.999 450 102] ^e	[-5.578]	f	$b^3\Sigma_u^+$
(1, -1, 0, 1)	[-0.999 445 835] ^e	[-9.844]	f	$b^3\Sigma_u^+$
(2, +1, 1, 1)	[-0.999 439 670] ^e	[-16.010]	f	$b^3\Sigma_u^+$

[1]: Pachucki & Komasa, JCP 130, 164113 (2009), [2]: Wolniewicz, Orlikowski, and Staszewska, JMS 238, 118 (2006),

[3]: Wolniewicz, MP 105, 1497 (2007).



singlet, para

even N , $p = +1$: $X^1\Sigma_g^+$
 odd N , $p = -1$: $B^1\Sigma_u^+$



triplet, ortho

even N , $p = +1$: $b^3\Sigma_u^+$
 odd N , $p = -1$: $a^3\Sigma_g^+$



singlet, ortho

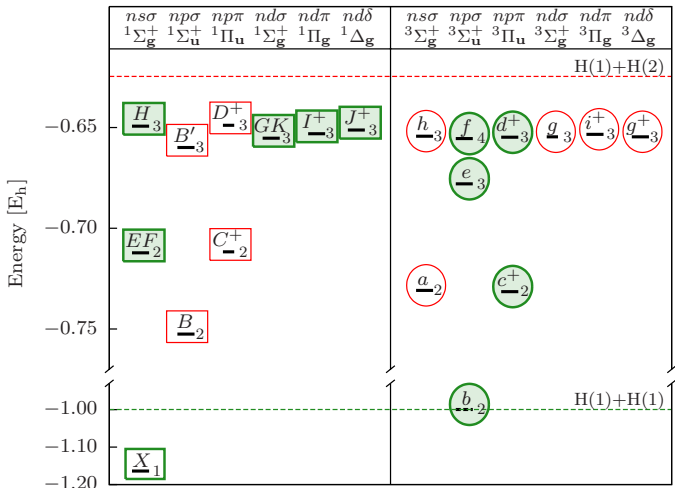
even N , $p = +1$: $B^1\Sigma_u^+$
 odd N , $p = -1$: $X^1\Sigma_g^+$



triplet, para

even N , $p = +1$: $a^3\Sigma_g^+$
 odd N , $p = -1$: $b^3\Sigma_u^+$

Orientation chart: electronic states of H₂



EM, J. Phys. Chem. A 117, 7195 (2013).

J. Brown and A. Carrington, Rotational Spectroscopy of Diatomic Molecules, Cambridge University Press, Cambridge (2003).

Towards the calculation of rovibronic resonances

Complex-coordinate rotation method

Complex coordinate rotation technique for the non-relativistic Coulomb Hamiltonian, $r \rightarrow re^{i\theta}$:

$$\hat{H} = \hat{T} + \hat{V} \rightarrow \hat{H}(\theta) = e^{-2i\theta} \hat{T} + e^{-i\theta} \hat{V} \quad (8)$$

Calculation of eigenvalues:

$$\mathbf{H}(\theta)\mathbf{v}(\theta)_i = E_i(\theta)\mathbf{S}\mathbf{v}(\theta)_i \quad (9)$$

which is replaced by

$$\mathbf{H}'(\theta)\mathbf{v}'(\theta)_i = E_i(\theta)\mathbf{v}'(\theta)_i \quad (10)$$

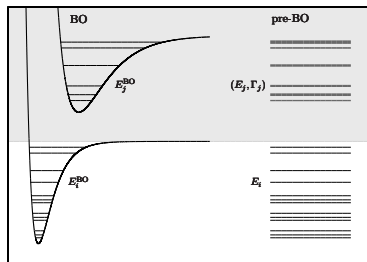
with

$$\begin{aligned} \mathbf{H}'(\theta) &= e^{-2i\theta} \mathbf{S}^{-1/2} \mathbf{T} \mathbf{S}^{-1/2} + e^{-i\theta} \mathbf{S}^{-1/2} \mathbf{V} \mathbf{S}^{-1/2} \\ &= \cos(2\theta) \mathbf{T}' + \cos(\theta) \mathbf{V}' - i(\sin(2\theta) \mathbf{T}' + \sin(\theta) \mathbf{V}') \end{aligned} \quad (11)$$

The complex symmetric eigenproblem is solved using LAPACK.

EM, J. Phys. Chem. A 117, 7195 (2013).

Motivation



Complex variational principle?

$Ps^- = \{e^+, e^-, e^-\}$ resonances

parameterization

- energy minimization
- random trials (sampling-importance sampling)
- it is easy to generate a reasonably good parameter set

Identified bound and resonance states for Ps^- (in E_h)

$(N, p, S_-)^b$	$\text{Re}(\mathcal{E})^c$	$\Gamma/2^c$	$\text{Re}(\mathcal{E}_{\text{Ref}})^c$	$\Gamma_{\text{Ref}}/2^c$	Ref.
(0, +1, 0)	-0.262 005 070 ^d	0 ^d	-0.262 005 070	0	[1]
(0, +1, 0)	-0.076 030 455	$2.152 \cdot 10^{-5}$	-0.076 030 442	$2.151 7 \cdot 10^{-5}$	[2]
(0, +1, 0)	-0.063 649 173	$4.369 \cdot 10^{-6}$	-0.063 649 175	$4.339 3 \cdot 10^{-6}$	[2]
(0, +1, 0)	-0.062 609	$2.5 \cdot 10^{-5}$	-0.062 550	$5.0 \cdot 10^{-7}$	[3]
(0, +1, 0)	-0.035 341 850	$3.730 \cdot 10^{-5}$	-0.035 341 885	$3.732 9 \cdot 10^{-5}$	[2]
(0, +1, 0)	-0.029 845 700	$2.781 \cdot 10^{-5}$	-0.029 846 146	$2.635 6 \cdot 10^{-5}$	[2]
(0, +1, 0)	-0.028 271	$1.8 \cdot 10^{-5}$	-0.028 200	$7.5 \cdot 10^{-6}$	[3]
(0, +1, 0)	-0.020 199 000	$8.800 \cdot 10^{-5}$	-0.020 213 921	$6.502 6 \cdot 10^{-5}$	[2]
(0, +1, 1)	-0.063 537 352	$2.132 \cdot 10^{-9}$	-0.063 537 354	$1.570 0 \cdot 10^{-9}$	[2]
(0, +1, 1)	-0.062 591	$2.6 \cdot 10^{-7}$	-0.062 550	$2.5 \cdot 10^{-10}$	[3]
(0, +1, 1)	-0.029 369 870	$1.300 \cdot 10^{-7}$	-0.029 370 687	$9.395 0 \cdot 10^{-8}$	[2]
(0, +1, 1)	-0.028 21	$1.9 \cdot 10^{-5}$	-0.028 05	$5.0 \cdot 10^{-8}$	[3]
(0, +1, 1)	-0.017 070 800	$6.710 \cdot 10^{-6}$	-0.017 101 172	$3.560 9 \cdot 10^{-7}$	[3]

$E(Ps(1)) = -1/4 = -0.25 E_h$, $E(Ps(2)) = -1/16 = -0.0625 E_h$ and $E(Ps(3)) = -1/36 = -0.0277 E_h$

[1]: Korobov, PRA 61, 064503 (2000), [2]: Li & Shakeshaft, PRA 71, 052505 (2005), [3]: Papp et al., Phys. Lett. A 304, 36 (2002).

$Ps_2 = \{e^+, e^+, e^-, e^-\}$ resonances

parameterization:

- energy minimization
- sampling-importance sampling

Identified bound and resonance states for Ps_2 (in E_h)

$(N, p, c)^b$	$(S_-, S_+)^c$	$\text{Re}(\mathcal{E})^d$	$\Gamma/2^d$	$\text{Re}(\mathcal{E}_{\text{Ref}})^d$	$\Gamma_{\text{Ref}}/2^d$	Ref.
(0, +1, +1)	(0, 0)	$-0.516\ 003\ 789\ 741^e$	0^e	$-0.516\ 003\ 790\ 416$	0	[1]
(0, +1, +1)	(0, 0)	$-0.329\ 38$	$3.03 \cdot 10^{-3}$	$-0.329\ 4$	$3.1 \cdot 10^{-3}$	[2]
(0, +1, +1)	(0, 0)	$-0.291\ 7$	$2.5 \cdot 10^{-3}$	$-0.292\ 4$	$1.95 \cdot 10^{-3}$	[2]
(0, +1, -1)	(0, 0)	$-0.314\ 677\ 072^e$	0^e	$-0.314\ 673\ 3$	0	[2]
(0, +1, -1)	(0, 0)	$-0.289\ 789\ 3$	$7.7 \cdot 10^{-5}$	$-0.289\ 76$	$7 \cdot 10^{-5}$	[2]
(0, +1, -1)	(0, 0)	$-0.279\ 25$	$2.3 \cdot 10^{-4}$	$-0.279\ 13$	$1 \cdot 10^{-4}$	[2]
(0, +1, +1)	(1, 1)	$-0.277\ 2$	$5.4 \cdot 10^{-4}$	$-0.276\ 55$	$1.55 \cdot 10^{-4}$	[2]
(0, +1, -1)	(1, 1)	$-0.309\ 0$	$5.7 \cdot 10^{-3}$	$-0.308\ 14$	$1.2 \cdot 10^{-4}$	[2]
(0, +1, -1)	(1, 1)	$-0.273\ 3$	$2.3 \cdot 10^{-3}$	$-0.273\ 6$	$8.5 \cdot 10^{-4}$	[2]
(0, +1, ± 1)	(1, 0)/(0, 1)	$-0.330\ 287\ 505^e$	0^e	$-0.330\ 276\ 81$	0	[2]
(0, +1, ± 1)	(1, 0)/(0, 1)	$-0.294\ 3$	$3.1 \cdot 10^{-3}$	$-0.293\ 9$	$2.15 \cdot 10^{-3}$	[2]
(0, +1, ± 1)	(1, 0)/(0, 1)	-0.282	$2 \cdot 10^{-3}$	$-0.282\ 2$	$8.5 \cdot 10^{-4}$	[2]

$E(Ps(1) + Ps(1)) = -1/2 = -0.5 E_h$ and $E(Ps(1) + Ps(2)) = -5/16 = -0.3125 E_h$

[1]: Bubin & Adamowicz, PRA 74, 052502 (2006), [2]: Suzuki & Usukura, Nucl. Inst. Meth. Phys. Res. B 221, 195 (2004).

Hunt for $H_2 = \{p^+, p^+, e^-, e^-\}$ resonances

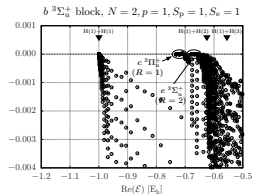
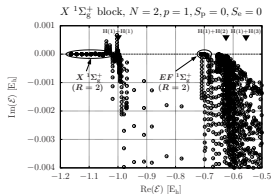
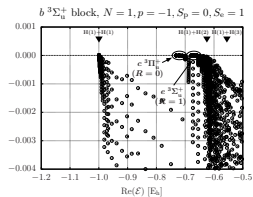
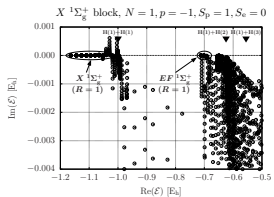
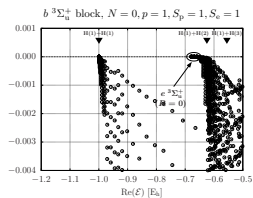
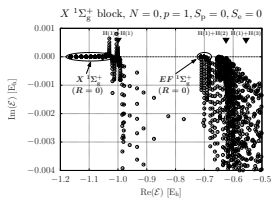
difficult to find a good parameter set, earlier strategies fail:

- energy minimization, sampling-importance sampling
- ✓ idea: parameter-transfer approach

Identified resonance states of H_2 embedded in the $b^3\Sigma_u^+$ continuum (in E_h)

$(N, p, S_p, S_e)^a$	$\text{Re}(\mathcal{E})^b$	$\Gamma/2^b$	$E_{\text{Ref,exp}}^c$	$E_{\text{Ref,theo}}^d$	Assignment ^e
(0, +1, 1, 1)	[-0.999 450 1] ^f [...]			[-0.999 455 7]	H(1)+H(1) continuum
(0, +1, 1, 1)	-0.677 947 1	$1 \cdot 10^{-7}$	-0.677 946 1	-0.677 942 7*	$e^3\Sigma_u^+, R=0, v=0$
(0, +1, 1, 1)	-0.668 549 3	$9 \cdot 10^{-7}$	-0.668 547 8	-0.668 541 0*	$e^3\Sigma_u^+, R=0, v=1$
(1, -1, 0, 1)	[-0.999 445 8] ^f [...]			[-0.999 455 7]	H(1)+H(1) continuum
(1, -1, 0, 1)	-0.731 434 0	$5 \cdot 10^{-7}$	-0.731 438 8	-0.731 469 1**	$c^3\Pi_u^+, R=0, v=0$
(1, -1, 0, 1)	-0.720 717 5	$2 \cdot 10^{-7}$	-0.720 782 6		$c^3\Pi_u^+, R=0, v=1$
(1, -1, 0, 1)	[...]				
(1, -1, 0, 1)	-0.677 705 5	$2 \cdot 10^{-7}$	-0.677 704 1	-0.677 698 2*	$e^3\Sigma_u^+, R=1, v=0$
(1, -1, 0, 1)	-0.668 319 5	$1 \cdot 10^{-6}$	-0.668 319 7	-0.668 309 8*	$e^3\Sigma_u^+, R=1, v=1$
(2, +1, 1, 1)	[-0.999 439 7] ^f [...]			[-0.999 455 7]	H(1)+H(1) continuum
(2, +1, 1, 1)	-0.730 888 2	$9 \cdot 10^{-7}$	-0.730 888 7		$c^3\Pi_u^+, R=1, v=0$
(2, +1, 1, 1)	-0.720 219 0	$< 2 \cdot 10^{-7}$	-0.720 258 0		$c^3\Pi_u^+, R=1, v=1$
(2, +1, 1, 1)	[...]				
(2, +1, 1, 1)	-0.677 222 9	$2 \cdot 10^{-8}$	-0.677 222 2		$e^3\Sigma_u^+, R=2, v=0$
(2, +1, 1, 1)	-0.667 863 2	$7 \cdot 10^{-7}$	-0.667 865 3		$e^3\Sigma_u^+, R=2, v=1$

^a Kotos & Rychlewski (1990), ^{**} Kotos & Rychlewski (1977), $E_{\text{Ref,exp}} = E_0 + T_{\text{exp}}$ with $E_0 = -1.164\,025\,030 E_h$ (g.s.)



Summary and outlook

Pre-Born–Oppenheimer Molecular Structure Theory

- **Quantum structure of molecules**

- On the Emergence of Molecular Structure**

- EM, J. Hutter, U. Müller-Herold, and M. Reiher, Phys. Rev. A 83, 052512 (2011).

- Extracting Elements of Molecular Structure from the All-Particle Wave Function**

- EM, J. Hutter, U. Müller-Herold, and M. Reiher, J. Chem. Phys. 135, 204302 (2011).

- **Approaching the non-relativistic limit for various quantum numbers**

- On the Calculation of Resonances in pre-Born–Oppenheimer Molecular Structure Theory**

- EM, J. Phys. Chem. A 117, 7195 (2013).

- Molecular Structure Calculations: a Unified Quantum Mechanical Description of Electrons and Nuclei using Explicitly Correlated Gaussian Functions and the Global Vector Representation**

- EM and M. Reiher, J. Chem. Phys. 137, 024104 (2012).

- **Towards a relativistic four-component pre-Born–Oppenheimer theory**

- Relativistic Kinetic-Balance Condition for Explicitly Correlated Basis Functions**

- B. Simmen, EM, and M. Reiher, J. Phys. B 48, 245004 (2015).

- Electric Transition Dipole Moment in pre-Born–Oppenheimer Molecular Structure Theory**

- B. Simmen, EM, and M. Reiher, J. Chem. Phys. 141, 154105 (2014).

- Elimination of the Translational Kinetic Energy Contamination in pre-Born–Oppenheimer Calculations**

- B. Simmen, EM, and M. Reiher, Mol. Phys. 111, 2086 (2013).

