Pre-Born–Oppenheimer Molecular Structure Theory

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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: (3\(n_n\) – 6)-dimensional representations

potential energy surface (PES)
Quantum chemistry and quantum mechanics

Born–Oppenheimer separation

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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.

Quantum chemistry and quantum mechanics

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- Kinetic energy operator:
  \[- \sum_{i=1}^{n_e} \frac{1}{2m_e} \Delta r_i\]
- Potential energy:
  \[\sum_{i=1}^{n_e} \sum_{j>i}^{n_e} \frac{1}{r_{ij}} - \sum_{i=1}^{n_e} \sum_{n=1}^{n_n} Z_n \]

Nuclear motion theory

- Translational and rotational invariance for an isolated molecule
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- Potential energy: \((3n_n - 6)\)-dimensional representations

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

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.

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

- a single $\langle r_{C-H} \rangle$ in an organic molecule

- linear or triangular $H_3^+$?
  $\langle \alpha_{HHH} \rangle = (0^\circ + 180^\circ + 0^\circ)/3 = 60^\circ$ 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

$\Rightarrow$ pre-Born–Oppenheimer theory

**Schrödinger equation**

$$\hat{H} \psi = E \psi \quad \text{with} \quad \hat{H}(m, q; r) = - \sum_{i=1}^{n_p+1} \frac{1}{2m_i} \Delta r_i + \sum_{i=1}^{n_p+1} \sum_{j>i}^{n_p+1} \frac{q_i q_j}{|r_i - r_j|} \tag{1}$$

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

**Pauli principle**

Spin statistics for fermions and bosons

$\Rightarrow$ spin: $s_i \ (i = 1, 2, \ldots, n_p + 1)$ parameters

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

$\Rightarrow$ 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
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 $\text{H}_2^+$ 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.
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
- equilibrium structure: local minimum structure of the PES
- we put in the molecular structure into this theoretical description

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);

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
- 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)?
  $\langle \alpha_{HHH} \rangle = (0^\circ + 180^\circ + 0^\circ)/3 = 60^\circ$ or $\langle \alpha_{HHH} \rangle = (60^\circ + 60^\circ + 60^\circ)/3 = 60^\circ$

⇒ problem: quantum mechanical indistinguishability of identical particles
Introduction

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

$$\rho_{P,a}(R_1) = \langle \psi(r)|\delta(r_a - r_P - R_1)|\psi(r)\rangle$$

(2)

2-particle density

$$D_{P,ab}^{(2)}(R_1, R_2) = \langle \psi(r)|\delta(r_a - r_P - R_1)\delta(r_b - r_P - R_2)|\psi(r)\rangle$$

(3)

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

(4)

On the emergence of molecular structure...

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

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

- charge-inversion symmetry
- mass-scale similarity

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

- bound for all \( m_a/m_b \) values [Martin et al., Phys. Rev. A 46, 3697 (1992)]
- let us consider the transition: \( H^- \rightarrow H_2^+ \)

Particle density vs. mass ratio

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

\[ N = 0, p = +1 \text{ (COM is at the middle of each plot) } \]

\[ \frac{m_a}{m_b} : 0.000543 \]

0.5

1

2

5

1840

H^-

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

Ps^-

\{e^-, e^-, e^+\}

H_2^+

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

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)

$\frac{m_a}{m_b} : \begin{array}{cccc}
0.000543 & 0.5 & 1 & 2 & 5 & 1840 \\
H^- & \text{Ps}^- & \text{H}_2^+ & \\
\{e^-, e^-, p^+\} & \{e^-, e^-, e^+\} & \{p^+, p^+, e^-\} & \\
\end{array}$

Superposition vs. rotating dumbbell

Radial and angular densities
\{a^\pm, a^\pm, b^\mp\}- and \{a^\pm, a^\pm, b^\mp, b^\mp\}-type systems

\begin{align*}
\frac{m_a}{m_b} & \begin{cases} 0.000543 \quad & H^- \\
1 & \quad & Ps^- \\
1840 & \quad & H_2^+ \\
0.000543 & \quad & H_2(e^-) \\
1 & \quad & Ps_2 \\
1840 & \quad & H_2(p^+) 
\end{cases}
\end{align*}

\rho_0, a
\rho_0, b
\Gamma_0, aa
\Gamma_0, bb

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

Radial and angular densities

\[ H_2D^+ = \{ e^-, e^-, p^+, p^+, d^+ \} \]

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

⇒ “molecular structure seen as correlation effects for the nuclei”
⇒ N.B. “traditional route”: introduce internal coordinates to describe nuclear motion...

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Molecules as few-particle quantum systems

⇒ pre-Born–Oppenheimer theory

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\]  

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

**Pauli principle**
Spin statistics for fermions and bosons
⇒ spin: \( s_i \) \((i = 1, 2, \ldots, n_p + 1)\) parameters

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

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

Adamowicz and co-workers, Suzuki and Varga
Molecules as few-particle quantum systems

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⇒ Variational solution with explicitly correlated Gaussians (ECGs)
Adamowicz and co-workers, Suzuki and Varga

⇒ Challenge: molecules with various quantum numbers
Introduction

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 \((S_a, M_{S_a}; S_b, M_{S_b}; ...)\)

- **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
  - flexible parameterization
- **analytic matrix elements**
- **generalized eigenvalue problem**, direct solution
  \((\sim 1000 \times 1000 \text{ real symmetric matrices})\)
- **variational principle**
  optimization of the basis function parameters (stochastic and Powell’s method)

Variational solution with explicitly correlated Gaussian functions

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- variational principle
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Symmetry-adapted basis functions

Basis function

\[ \phi^{(\lambda)}(\mathbf{r}; \mathbf{A}, \mathbf{u}, K) = |\mathbf{v}|^{2K+N} Y_{N}^{M,N}(\hat{\mathbf{v}}) \exp \left( -\frac{1}{2} \sum_{i=1}^{n_p+1} \sum_{j>i}^{n_p+1} \alpha_{ij}(\mathbf{r}_i - \mathbf{r}_j)^2 \right) \]

with \[ \mathbf{v} = \sum_{i=1}^{n_p+1} u_i \mathbf{r}_i \]

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

Basis-set expansion

\[ \psi_{0}^{(\lambda,s)} = c_1 \hat{A}\{\chi^{(s)}_{1}\phi^{(\lambda)}(\mathbf{r}; \{\alpha_{ij,1}, u_{i,1}, K_1\})\} + c_2 \hat{A}\{\chi^{(s)}_{2}\phi^{(\lambda)}(\mathbf{r}; \{\alpha_{ij,2}, u_{i,2}, K_2\})\} + c_3 \hat{A}\{\chi^{(s)}_{3}\phi^{(\lambda)}(\mathbf{r}; \{\alpha_{ij,3}, u_{i,3}, K_3\})\} + \ldots \]

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

$$\Psi(A') = \sum_{I=1}^{N_b} c_I \Phi_I(A')[P_I(A)]$$
Introduction

Test case: $\text{H}_2^+ = \{p^+, p^+, e^-\}$

Energy levels and dissociation energies (examples)

<table>
<thead>
<tr>
<th>$N$</th>
<th>$p$</th>
<th>$S_p$</th>
<th>$E / E_h$</th>
<th>$D / \text{cm}^{-1}$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>$-0.499731516(7)$</td>
<td>0.807(1)</td>
<td>$\tilde{A}^2\Sigma_u^+$, $\nu = 0$; ortho</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$-0.597139060(4)$</td>
<td>21379.290(2)</td>
<td>$\tilde{X}^2\Sigma_g^+$, $\nu = 0$; para</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Energy, $E$: $EH$; Dissociation energy, $D$: $cm^{-1}$

H₂ = \{p^+, p^+, e^-, e^-\}

parameterization:
- sampling-importance sampling and Powell’s method for fine-tuning
- parameter-transfer approach

Calculated energy levels of H₂ with \(N = 0, 1, 2\) total (orbital plus rotational) angular momentum quantum number

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

\(H_2 = \{p^+, p^+, e^-, e^-\}\)
Orientation chart: electronic states of $\text{H}_2$


Towards the calculation of rovibronic resonances

**Complex-coordinate rotation method**

Complex coordinate rotation technique for the non-relativistic Coulomb Hamiltonian, \( \mathbf{r} \rightarrow \mathbf{r} e^{i\theta} \):

\[
\hat{H} = \hat{T} + \hat{V} \rightarrow \hat{H}(\theta) = e^{-2i\theta} \hat{T} + e^{-i\theta} \hat{V} \tag{8}
\]

Calculation of eigenvalues:

\[
H(\theta)\mathbf{v}(\theta)_i = E_i(\theta)S\mathbf{v}(\theta)_i \tag{9}
\]

which is replaced by

\[
H'(\theta)\mathbf{v}'(\theta)_i = E_i(\theta)\mathbf{v}'(\theta)_i \tag{10}
\]

with

\[
H'(\theta) = e^{-2i\theta} S^{-1/2} TS^{-1/2} + e^{-i\theta} S^{-1/2} VS^{-1/2} = \cos(2\theta) T' + \cos(\theta) V' - i(\sin(2\theta) T' + \sin(\theta) V') \tag{11}
\]

The complex symmetric eigenproblem is solved using LAPACK.

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

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

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

$E(\text{Ps}(1)) = -1/4 = -0.25 E_h$, $E(\text{Ps}(2)) = -1/16 = -0.062 5 E_h$ and $E(\text{Ps}(3)) = -1/36 = -0.027 7 E_h$


**Ps$_2$ = \{e^+, e^+, e^-, e^-\} resonances**

Parameterization:
- Energy minimization
- Sampling-importance sampling

Identified bound and resonance states for Ps$_2$ (in E$_h$)

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

$E(Ps(1) + Ps(1)) = -1/2 = -0.5$ E$_h$ and $E(Ps(1) + Ps(2)) = -5/16 = -0.312 5$ E$_h$


---

*Edit Mátéyus (ELTE)*
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 $E_h$)

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

* Kołos & Rychlewski (1990), ** Kołos & 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
  - Extracting Elements of Molecular Structure from the All-Particle Wave Function

- **Approaching the non-relativistic limit for various quantum numbers**
  - On the Calculation of Resonances in pre-Born–Oppenheimer Molecular Structure Theory
  - Molecular Structure Calculations: a Unified Quantum Mechanical Description of Electrons and Nuclei using Explicitly Correlated Gaussian Functions and the Global Vector Representation

- **Towards a relativistic four-component pre-Born–Oppenheimer theory**
  - Relativistic Kinetic-Balance Condition for Explicitly Correlated Basis Functions
  - Electric Transition Dipole Moment in pre-Born–Oppenheimer Molecular Structure Theory
  - Elimination of the Translational Kinetic Energy Contamination in pre-Born–Oppenheimer Calculations