On the computational limits of a full quantum mechanical treatment for few-body systems

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The dimension of the problem

Finding a very accurate approximation to the exact full quantum wave function

- The few-body problem is treated without any assumptions.
- Fine description of particle correlation with basis functions depending explicitly on the interparticle distances:

Explicitly Correlated Gaussians (ECGs)
with general vector representation (GVR)

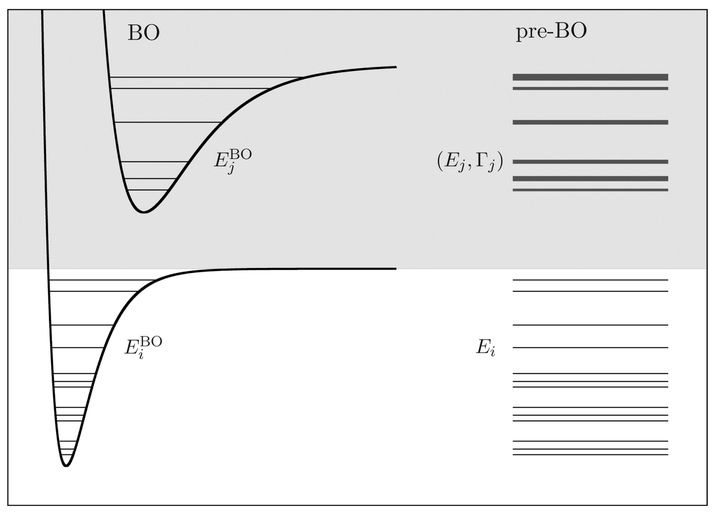
$$\phi_k = |\boldsymbol{v}|^{2K+L} Y_{LM_L}(\boldsymbol{v}) \exp\left[-\boldsymbol{r}^T (\boldsymbol{A}_k \otimes \boldsymbol{I}_3)\, \boldsymbol{r}\right] \quad (1)$$

1. Non linear optimization problem for the elements of the $\boldsymbol{A}$ correlation matrix, the $\boldsymbol{u}$ vector and K
2. These trial basis functions must become a complete set in the infinite dimension limit
3. Efficiently solvable analytical integrals required

- More difficulties for excited states and for larger systems:

1. The representation of the orbital part of the total wave function becomes rapidly high involved
2. Imposing the correct permutation symmetry for set of identical particles largely increases the number of integral evaluations

Rovibrational levels of a dihydrogen system



Imposing the correct permutation symmetry

Given the permutation group S_n relative to a system made up of n identical particles, the wave functions must be a simultaneous eigenfunctions of both the Hamiltonian and U_π, a representation of $\pi \in S_n$, since $[H, U_\pi] = 0$.

It is therefore necessary to project the basis functions onto the appropriate irreducible representation of the permutation group:

$$\hat{\mathcal{A}} = (N_{perm})^{-1/2} \sum_{\pi \in S_n} \varepsilon_\pi \hat{\pi}, \quad (8)$$

where ε_π is equal to $(-1)^p$ if the identical particles are fermions or to 1 if bosons.
The symmetrized form of the ECG-GVR basis function is then written as

$$\Phi_k = \hat{A}\phi_k = (N_{perm})^{-1/2} \sum_{\pi \in S_n} \varepsilon_\pi \exp\left[-\boldsymbol{r}^T \left(U_\pi^T \boldsymbol{A}_k U_\pi \otimes \boldsymbol{I}_3\right) \boldsymbol{r}\right], \quad (9)$$

so as the matrix elements of a spin independent and permutationally invariant operator, $\hat{O}$, become

$$\begin{aligned} O_{ij} &= \left\langle \hat{\mathcal{A}}\left[\phi_i\, \chi_i\right] \middle| \hat{O} \middle| \hat{\mathcal{A}}\left[\phi_i\, \chi_j\right] \right\rangle = \left\langle \phi_i\, \chi_i \middle| \hat{\mathcal{A}}^\dagger \hat{O} \hat{\mathcal{A}} \middle| \phi_i\, \chi_j \right\rangle = \left\langle \phi_i\, \chi_i \middle| \hat{O}\hat{\mathcal{A}}\hat{\mathcal{A}} \middle| \phi_i\, \chi_j \right\rangle \\ &= (N_{perm})^{1/2} \left\langle \phi_i\, \chi_i \middle| \hat{O} \middle| \hat{\mathcal{A}}\phi_i\, \chi_j \right\rangle = \sum_{\pi \in S_n} \varepsilon_\pi \left\langle \phi_i\, \chi_i \middle| \hat{O} \middle| \hat{\pi}\left[\phi_j\, \chi_j\right] \right\rangle = \sum_{\pi \in S_n} T_{ij}^\pi O_{ij}^\pi \end{aligned} \quad (10)$$

where

$$T_{ij}^\pi = \left\langle \chi_i \middle| \hat{O} \middle| \hat{\pi}\, \chi_j \right\rangle \qquad O_{ij}^\pi = \varepsilon_\pi \left\langle \phi_i \middle| \hat{O} \middle| \hat{\pi}\, \phi_j \right\rangle \quad (11)$$

For systems with different subsets of identical particles the projection operators for irreducible representations of the symmetric group are called Young operators, $\hat{Y} = \hat{S}\hat{A}$, where

$$\hat{A} = \prod_m \hat{A}_m \qquad \hat{S} = \prod_n \hat{S}_n \quad (12)$$

and are the product of antisymmetrizers over each column and the product of symmetrizers over each row of the associated Young diagram.

Scaling Analysis

$$n_p = number\ of\ particles$$
$$N_{\text{ECG-GVR}} = number\ of\ basis\ functions\ \phi_k$$

ECG-GVR function $\longrightarrow (n_p + 1)(n_p + 2)/2$ free parameters

Each optimization step requires:

1. Random variation of the parameters for one or more ϕ_k
2. Evaluation of the matrix elements for the operators: $\hat{S}$, $\hat{T}$ and $\hat{V}$
3. Löwdin orthonormalization algorithm $\left(\propto {N_{\text{ECG-GVR}}}^3\right)$
4. Diagonalization of the Hamiltonian $\left(\propto {N_{\text{ECG-GVR}}}^3\right)$

Antisymmetrization

The number of integral evaluations grows factorially with respect to the number of each subset of identical particles

H_2^+:	$2! \cdot 1!$	$= 2$
H_2:	$2! \cdot 2!$	$= 4$
H_3^+:	$3! \cdot 2!$	$= 12$
H_3:	$3! \cdot 3!$	$= 36$
H_2O:	$2! \cdot 1! \cdot 10!$	$= 7257600$

Time required for every step scaled with respect to the diagonalization process in that row.
Each integral evaluation time must be multiplied by corresponding factorials as explained above.

	$N_{\text{ECG-GVR}}$	K_{max}	$\hat{S}$	$\hat{T}$	$\hat{V}$	$\hat{V}_{128bit}$	*Löwdin*	*Diagonalization*
H_2	100	0	0.004	0.005	0.011	0.024	0.996	1
	1000	0	0.000	0.000	0.000	0.000	0.925	1
	100	10	0.005	0.006	0.734	8.423	0.922	1
H_3^+	100	0	0.021	0.027	0.047	0.088	0.974	1
	100	10	0.021	0.026	1.311	14.40	0.994	1

Pre-Born-Oppenheimer theory: background

The non-relativistic Hamiltonian is obtained by separating out the motion of the center of mass.
Starting from an $n+1$ particles Hamiltonian

$$\hat{H} = -\sum_{i=1}^{n+1} \frac{1}{2M_i} \triangle_{\boldsymbol{r}_i} + \sum_{i=1}^{n+1} \sum_{j>i}^{n+1} \frac{q_i q_j}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}, \quad (2)$$

the internal coordinates can be separated from the translational invariant part with the action of an appropriate unitary transformation:

$$\begin{aligned} \hat{H} = &\underbrace{-\frac{1}{2m_{tot}} \triangle_{\boldsymbol{x}_{CM}}}_{\hat{T}_{CM}} \\ &\underbrace{-\sum_{i=1}^{n} \sum_{j=1}^{n} \boldsymbol{\mu}_{ij} \boldsymbol{\nabla}_{\boldsymbol{x_i}}^T \boldsymbol{\nabla}_{\boldsymbol{x}_j} + \sum_{i=1}^{n} \sum_{j>i}^{n} \frac{q_i q_j}{\left|\left(\boldsymbol{f}_{ij}^{(x)} \otimes \boldsymbol{1}_3\right)^T \boldsymbol{x}\right|}}_{\hat{H}_{TI}} \end{aligned} \quad (3)$$

where μ_{ij} is the reduced mass and $\boldsymbol{f}_{ij}$ is related to the transformation matrix: $(f_{ij})_k = \boldsymbol{U}_{ik} - \boldsymbol{U}_{jk}$.

Combining the spatial part ϕ^{L,M_L} with the spin function χ^{S,M_S} relative to the desired spin quantum numbers one can write the approximate state function:

$$\Psi(\boldsymbol{r}) = \sum_{k=1}^{N} c_k \hat{A}\left[\phi_k^{L,M_L}(\boldsymbol{r}; \boldsymbol{v_k}, \boldsymbol{A}_k, K) \chi_k^{S,M_S}\right] \quad (4)$$

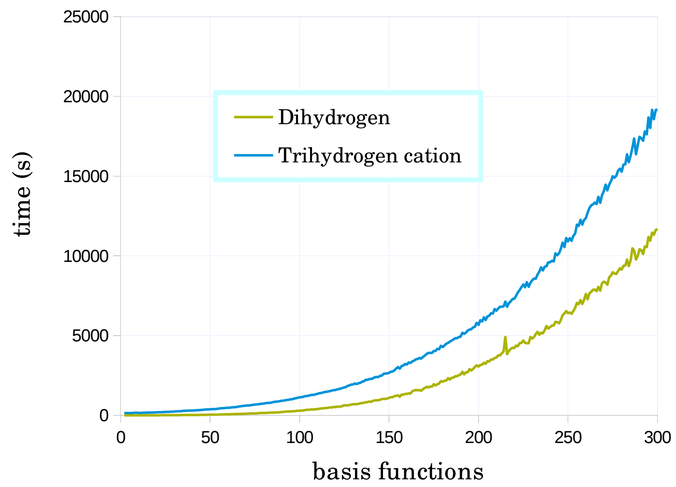
Minimization of the energy

1. The elements of $\boldsymbol{A}_k$ require a non-linear optimization process
2. The linear expansion coefficients c_k lead to the generalized eigenproblem:
$$\boldsymbol{HC} = \boldsymbol{ESC} \quad (5)$$
where $\boldsymbol{H}$ and $\boldsymbol{S}$ are the matrix representation of the Hamiltonian and the overlap:

$$\boldsymbol{H}_{ij} = \left\langle \hat{A}\left[\phi_i^{L,M_L} \chi_i^{S,M_S}\right] \middle| \hat{H} \middle| \hat{A}\left[\phi_j^{L,M_L} \chi_j^{S,M_S}\right] \right\rangle \quad (6)$$
$$\boldsymbol{S}_{ij} = \left\langle \hat{A}\left[\phi_i^{L,M_L} \chi_i^{S,M_S}\right] | \hat{A}\left[\phi_j^{L,M_L} \chi_j^{S,M_S}\right] \right\rangle \quad (7)$$

Rovibrational ground states calculations

Scaling of calculations on a four- and five-particle systems, H_2 and H_3^+ respectively



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