High precision calculations on small atoms and molecules using explicitly correlated Gaussians

Sergiy Bubin[1] and Ludwik Adamowicz[2]

[1] *Department of Physics, Nazarbayev University*

[2] *Department of Chemistry and Biochemistry, University of Arizona*

PSAS 2016, Jerusalem

Republic of Kazakhstan

Quick facts

9-th largest country in the world by territory

Population: $\sim$ 18M

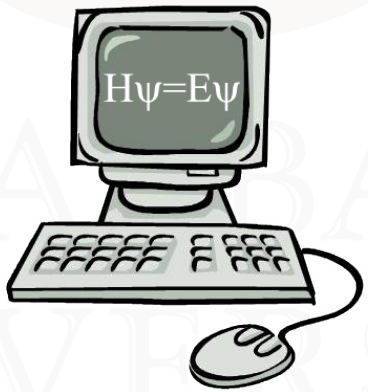
Capital: Astana (since 1997)


NAZARBAYEV UNIVERSITY

- Theoretical spectroscopy
- Possibility of determining fundamental constants (e.g. fine-structure constant), nuclear radii, quadrupole moments, etc.
- Stability of exotic systems (e.g. positron-atom complexes)
- Reference for testing less accurate (yet computationally inexpensive) approaches

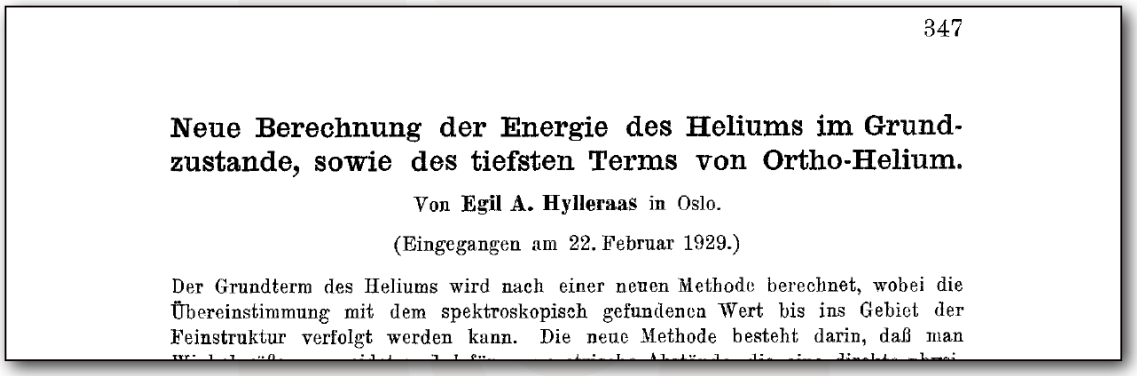
- Steep effort scaling upon increasing the number of particles
- Steep effort scaling upon increasing the basis size
- Slow convergence of orbital-based methods
- Excited states are often difficult
- DFT: inexpensive, but no systematic way to improve accuracy

Spectroscopic accuracy is currently out of reach for traditional electronic structure methods



Explicit correlation: r_{ij} terms

- In 1929 Hylleraas included terms that depend on interelectronic distances (r_{12}) in the trial wavefunction of He



347

Neue Berechnung der Energie des Heliums im Grundzustande, sowie des tiefsten Terms von Ortho-Helium.

Von **Egil A. Hylleraas** in Oslo.

(Eingegangen am 22. Februar 1929.)

Der Grundterm des Heliums wird nach einer neuen Methode berechnet, wobei die Übereinstimmung mit dem spektroskopisch gefundenen Wert bis ins Gebiet der Feinstruktur verfolgt werden kann. Die neue Methode besteht darin, daß man

Die neue Methode besteht nun darin, daß die drei in dem Ausdruck für die potentielle Energie direkt vorkommenden Größen r_1, r_2, r_{12} als unabhängige Variable gewählt werden, statt früher r_1, r_2, und ϑ, der Winkel zwischen r_1 und r_2.

Wir machen also den Ansatz

$$\left.\begin{aligned} \psi &= \psi(r_1, r_2, r_{12}), \\ r_1^2 &= x_1^2 + y_1^2 + z_1^2, \\ r_2^2 &= x_2^2 + y_2^2 + z_2^2, \\ r_{12}^2 &= (x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2, \end{aligned}\right\} \qquad (3)$$

- In 1960 Boys and Singer proposed a simpler form: Gaussian (exponential quadratic) functions of r_{ij}

$$e^{-\alpha R_{12}^2 - \beta R_{13}^2 \ldots - \gamma R_{N,N-1}^2}$$

- One of the most powerful approaches to solve quantum few-body problem
- Diverse areas of applicability (atomic, molecular, nuclear, condensed-matter physics)
- Matrix elements can be evaluated analytically for arbitrary N
- Variational principle, reliability
- Excited states are usually not a problem
- Very accurate and flexible

$$
\begin{aligned}
\phi_k &= \exp[-\lambda_{12}^{(k)} R_{12}^2 - \ldots - \lambda_{N,N-1}^{(k)} R_{N,N-1}^2] \\
&= \exp[-\alpha_1^{(k)} r_1^2 - \ldots - \alpha_n^{(k)} r_n^2 - \beta_{1,2}^{(k)} \mathbf{r}_1' \mathbf{r}_2 - \ldots - \beta_{n-1,n}^{(k)} \mathbf{r}_{n-1}' \mathbf{r}_n] \\
&= \exp[-\mathbf{r}' (A_k \otimes I_3)\, \mathbf{r}]
\end{aligned}
$$

$$
\mathbf{r} = \begin{bmatrix} \mathbf{r}_1 \\ \mathbf{r}_2 \\ \vdots \\ \mathbf{r}_n \end{bmatrix} = \begin{bmatrix} \mathbf{R}_2 - \mathbf{R}_1 \\ \mathbf{R}_3 - \mathbf{R}_1 \\ \vdots \\ \mathbf{R}_N - \mathbf{R}_1 \end{bmatrix}, \quad A_k = \begin{bmatrix} (A_k)_{11} & (A_k)_{12} & \cdots & (A_k)_{1n} \\ (A_k)_{21} & (A_k)_{22} & \cdots & (A_k)_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ (A_k)_{n1} & (A_k)_{n2} & \cdots & (A_k)_{nn} \end{bmatrix}
$$

$$
n = N - 1, \qquad I_3 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}
$$

$$L = 1,\ M = 0: \quad \phi_k = z_{i_k} \exp[-\mathbf{r}'(A_k \otimes I_3)\,\mathbf{r}]$$

$$L = 2,\ M = 0: \quad \phi_k = (x_{i_k} x_{j_k} + y_{i_k} y_{j_k} - 2 z_{i_k} z_{j_k}) \exp[-\mathbf{r}'(A_k \otimes I_3)\,\mathbf{r}]$$

For large L it becomes complicated. Suzuki-Varga recipe:

$$\phi_k = \theta_{LM}(\mathbf{r}) \exp(-\mathbf{r}'(A_k \otimes I_3)\mathbf{r}). \tag{1}$$

$$\theta_{LM}(\mathbf{r}) = v^{2K+L} Y_{LM}(\hat{\mathbf{v}}), \tag{2}$$

where

$$\mathbf{v} = \sum_{i=1}^{n} u_i \mathbf{r}_i, \tag{3}$$

$v = |\mathbf{v}|$, and Y_{LM} is the usual spherical harmonic.

Hamiltonian of a Coulombic system:

$$H = -\sum_{i=1}^{N} \frac{1}{2M_i} \nabla_i^2 + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{Q_i Q_j}{R_{ij}}, \tag{4}$$

where

$\mathbf{R}_i$ are particle coordinates in lab frame,

$R_{ij} = |\mathbf{R}_j - \mathbf{R}_i|$ are interparticle distances.

Relativistic and QED effects can be included perturbatively:

$$E_{\text{tot}} = E_{\text{nonrel}} + \alpha^2 E_{\text{rel}}^{(2)} + \alpha^3 E_{\text{QED}}^{(3)} + \dots$$

$$H_{\text{rel}} = H_{\text{MV}} + H_{\text{D}} + H_{\text{OO}} + H_{\text{SO}} + H_{\text{SS}} + H_{\text{A}}$$

Rayleigh-Ritz scheme:

$$\psi = \sum_{k=1}^{K} c_k \varphi_k, \tag{5}$$

where $\{\varphi_k(\mathbf{r}_1, \ldots, \mathbf{r}_n)\}$ is some set of basis functions.

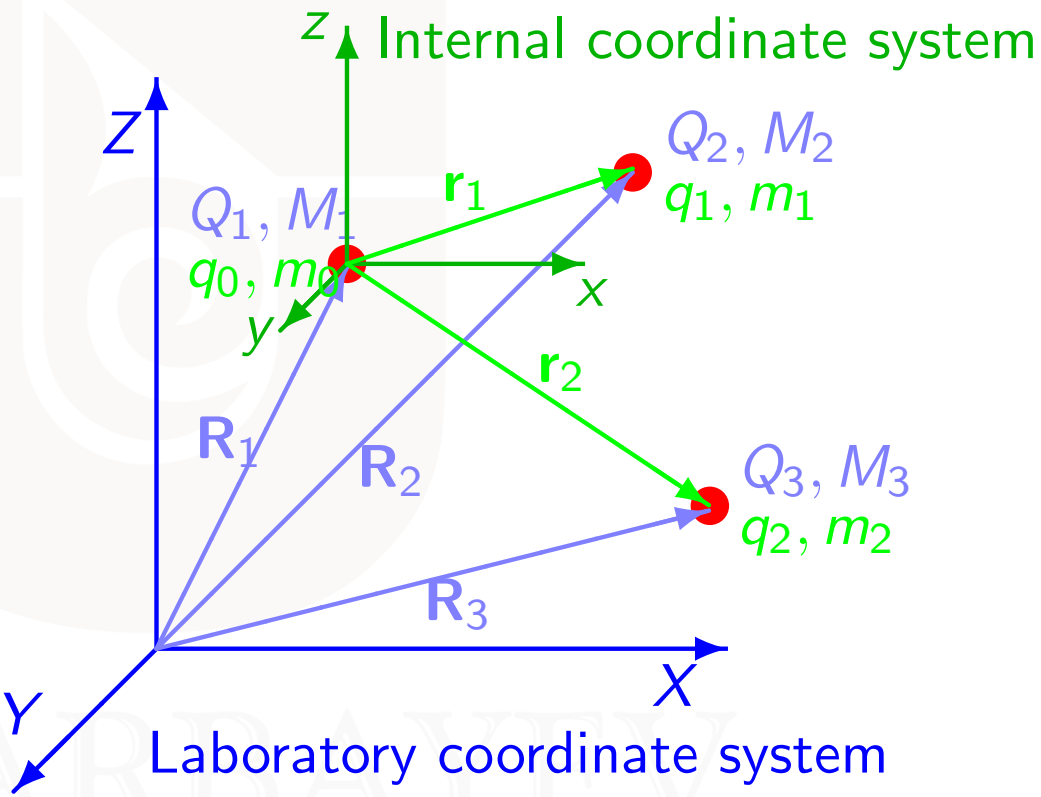
Generalized Symmetric Eigenvalue Problem:

$$Hc = \varepsilon Sc, \tag{6}$$

with

$$H_{kl} = \langle \varphi_k | H | \varphi_l \rangle \qquad S_{kl} = \langle \varphi_k | \varphi_l \rangle.$$

$$
\begin{aligned}
\mathbf{r}_0 &= \frac{M_1}{M_{\text{tot}}}\mathbf{R}_1 + \frac{M_2}{M_{\text{tot}}}\mathbf{R}_2 + \ldots + \frac{M_N}{M_{\text{tot}}}\mathbf{R}_N, \\
\mathbf{r}_1 &= -\mathbf{R}_1 + \mathbf{R}_2, \\
\mathbf{r}_2 &= -\mathbf{R}_1 + \mathbf{R}_3, \\
&\vdots \\
\mathbf{r}_n &= -\mathbf{R}_1 + \mathbf{R}_N,
\end{aligned}
$$



Kinetic energy: $T_{\text{tot}} = T_{\text{CM}} + T_{\text{int}}$

$$\psi_{\text{tot}}(\mathbf{r}) = \exp(-i\mathbf{k}_0 \cdot \mathbf{r}_0)\psi_{\text{int}}(\mathbf{r}_1, \ldots, \mathbf{r}_n) \qquad (7)$$

If n identical particles

$$\varphi_k = \hat{Y}\phi_k = \sum_{t=1}^{n!} \gamma_t \hat{P}_t \phi_k \tag{8}$$

Spin-free formalism, Young tableaux

1	2
3	4
5	

(9)

$$\hat{Y} = (1 - \hat{P}_{24})(1 - \hat{P}_{13})(1 - \hat{P}_{15} - \hat{P}_{35})(1 + \hat{P}_{12})(1 + \hat{P}_{34}) \tag{10}$$

Action of a single permutation operator on primitive ECGs:

$$\hat{P} \exp\left[-\mathbf{r}' A_k \mathbf{r}\right] = \exp\left[-(P\mathbf{r})' A_k (P\mathbf{r})\right] = \exp\left[-\mathbf{r}'(P' A_k P)\mathbf{r}\right] \tag{11}$$

Flexibility comes from the multitude of nonlinear parameters

- Optimization of 10k-100k parameters is required
- Stochastic Variational Method (Kukulin and Krasnopol'sky; Varga and Suzuki)
- Analytic energy gradient

$$\mathsf{Hc} = \varepsilon \mathsf{Sc}$$

$$\frac{\partial \varepsilon}{\partial \alpha} = \mathsf{c}^{\dagger} \left(\frac{\partial \mathsf{H}}{\partial \alpha} - \varepsilon \frac{\partial \mathsf{S}}{\partial \alpha} \right) \mathsf{c}$$

Need to evaluate $\frac{\partial \mathsf{H}_{kl}}{\partial \mathrm{vech} L_k}$, $\frac{\partial \mathsf{S}_{kl}}{\partial \mathrm{vech} L_k}$, where $A_k = L_k L_k^T$

Total nonrelativistic energies of $^{\infty}$He and $^{\infty}$Li.

Atom(state)	Method	Basis size	Energy (a.u.)
He($1s^2$)	CI[a]	8 586	−2.903 712 786
	ECG	1 000	−2.903 724 377 033 2
	HYL-LOG[b]	24 099	−2.903 724 377 034 119 598...
Li($1s^2 2s$)	CI[c]		−7.478 025 4
	ECG[d]	10 000	−7.478 060 323 81
	ECG	3 600	−7.478 060 323 884 4
	HYL[e]	3 910	−7.478 060 323 880 9
	HYL[e]	26 520	−7.478 060 323 910 134 843
Li($1s^2 2p$)	ECG	3 600	−7.410 156 532 553 2
	HYL[e]	4 824	−7.410 156 532 310 89
	HYL[e]	30 224	−7.410 156 532 650 66

[a] M. W. J. Bromley and J. Mitroy, Int. J. Quantum Chem. **107**, 1150 (2007).
[b] C. Schwartz, Int. J. Mod. Phys. E **15**, 877 (2006) ; arXiv:math-ph/0605018 (2006).
[c] O. Jitrik and C. Bunge, Phys. Rev. A 56, 2614 (1997).
[d] M. Stanke, J. Komasa, D. Kedziera, S. Bubin, and L. Adamowicz, Phys. Rev. A 78, 052507 (2008).
[e] L. M. Wang , Z.-C. Yan, H. X. Qiao, G. W. F. Drake, Phys. Rev. A **83**, 034503 (2011).

- Expectation values of singular operators, e.g. $\delta(\mathbf{r}_i - \mathbf{r}_j)$, coverge slowly
- Expectation value identities (e.g. Drachman or Hiller-Sucher-Feinberg) can help circumvent the problem

$$\langle\psi|\tilde{\delta}(\mathbf{R}_{ij})|\psi\rangle =$$

$$= \frac{1}{2\pi}\frac{M_i M_j}{M_i+M_j}\left[\langle\psi|\frac{2}{R_{ij}}(E-V)|\psi\rangle - \sum_{k=1}^{N}\frac{1}{M_k}\langle\boldsymbol{\nabla}_{\mathbf{R}_k}\psi|\frac{1}{R_{ij}}|\boldsymbol{\nabla}_{\mathbf{R}_k}\psi\rangle\right]$$

$$\langle\psi|\tilde{\delta}(\mathbf{r}_{ij})|\psi\rangle =$$

$$= \frac{1}{2\pi}\frac{1}{\mathrm{tr}[MJ_{ij}]}\left[\langle\psi|\frac{1}{r_{ij}}(E-V)|\psi\rangle - \langle\boldsymbol{\nabla}_{\mathbf{r}}\psi|\frac{1}{r_{ij}}\mathbf{M}|\boldsymbol{\nabla}_{\mathbf{r}}\psi\rangle\right]$$

R. J. Drachman, J. Phys. B **14**, 2733 (1981);

K. Pachucki, W. Cencek, and J. Komasa, J. Chem. Phys. **122**, 184101 (2005).

- Two most demanding tasks (evaluation of matrix elements and solving the eigenvalue problem) can be parallelized efficiently.
- Message Passing Interface for parallel computations
- Several choices for precision (double, extended, quadruple)
- Checkpointing

Short history of high-precision calculations of small atoms (ground state) - reaching $\sim 10^{-10}$ relative accuracy

- He - 1960s (Pekeris *et al.*)
- Li - first half of 1990s (Drake *et al.*)
- Be - 2009
- B - ???

Energies and expectation values for the lowest four ^2S states of Boron. All values are in atomic units.

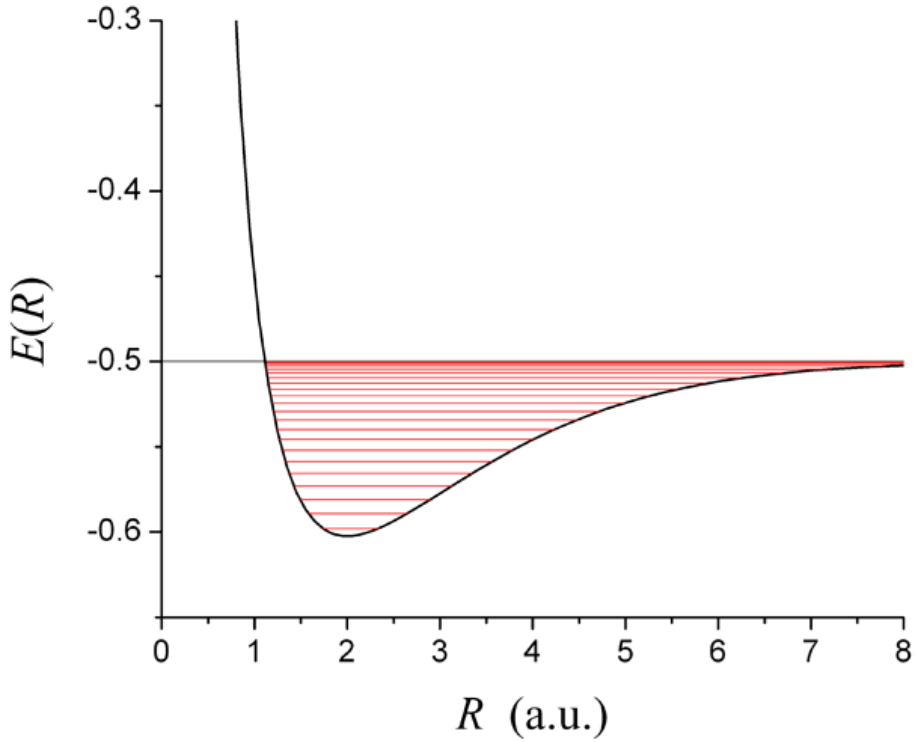
System	Basis size	E_{nr}	$\langle \tilde{H}_{\mathrm{MV}} \rangle$	$\langle \tilde{\delta}(\mathbf{r}_i) \rangle$	$\langle \tilde{\delta}(\mathbf{r}_{ij}) \rangle$	$\langle H_{\mathrm{OO}} \rangle$	$\langle \mathcal{P}(1/r_i^3) \rangle$
^{11}B, $2s^2 3s$	12000	-24.470143683	-700.2215	14.5067753	0.3581634	-1.554458	-417.503
	13000	-24.470143701	-700.2213	14.5067753	0.3581634	-1.554457	-417.514
	14000	-24.470143716	-700.2213	14.5067753	0.3581634	-1.554457	-417.515
^{11}B, $2s^2 4s$	12000	-24.401943300	-699.5609	14.4957254	0.3576671	-1.551909	-417.134
	13000	-24.401943358	-699.5609	14.4957253	0.3576671	-1.551908	-417.149
	14000	-24.401943402	-699.5609	14.4957252	0.3576671	-1.551907	-417.154
^{11}B, $2s^2 5s$	12000	-24.378547281	-699.0707	14.4867601	0.3573244	-1.537170	-416.674
	13000	-24.378547448	-699.0706	14.4867591	0.3573243	-1.537166	-416.776
	14000	-24.378547580	-699.0705	14.4867581	0.3573243	-1.537162	-416.782
^{11}B, $2s^2 6s$	12000	-24.367923986	-697.3405	14.4539583	0.3561555	-1.464967	-415.330
	13000	-24.367924540	-697.3399	14.4539512	0.3561553	-1.464945	-415.464
	14000	-24.367924960	-697.3395	14.4539458	0.3561551	-1.464929	-415.473

Computed $ns \rightarrow 3s$ transition frequencies (in cm^{-1}) for ^{11}B in comparison with the experimental values. The subscript (nr, $\mathrm{nr}+\mathrm{rel}$, or $\mathrm{nr}+\mathrm{rel}+\mathrm{QED}$) indicates the inclusion of relativistic and QED corrections.

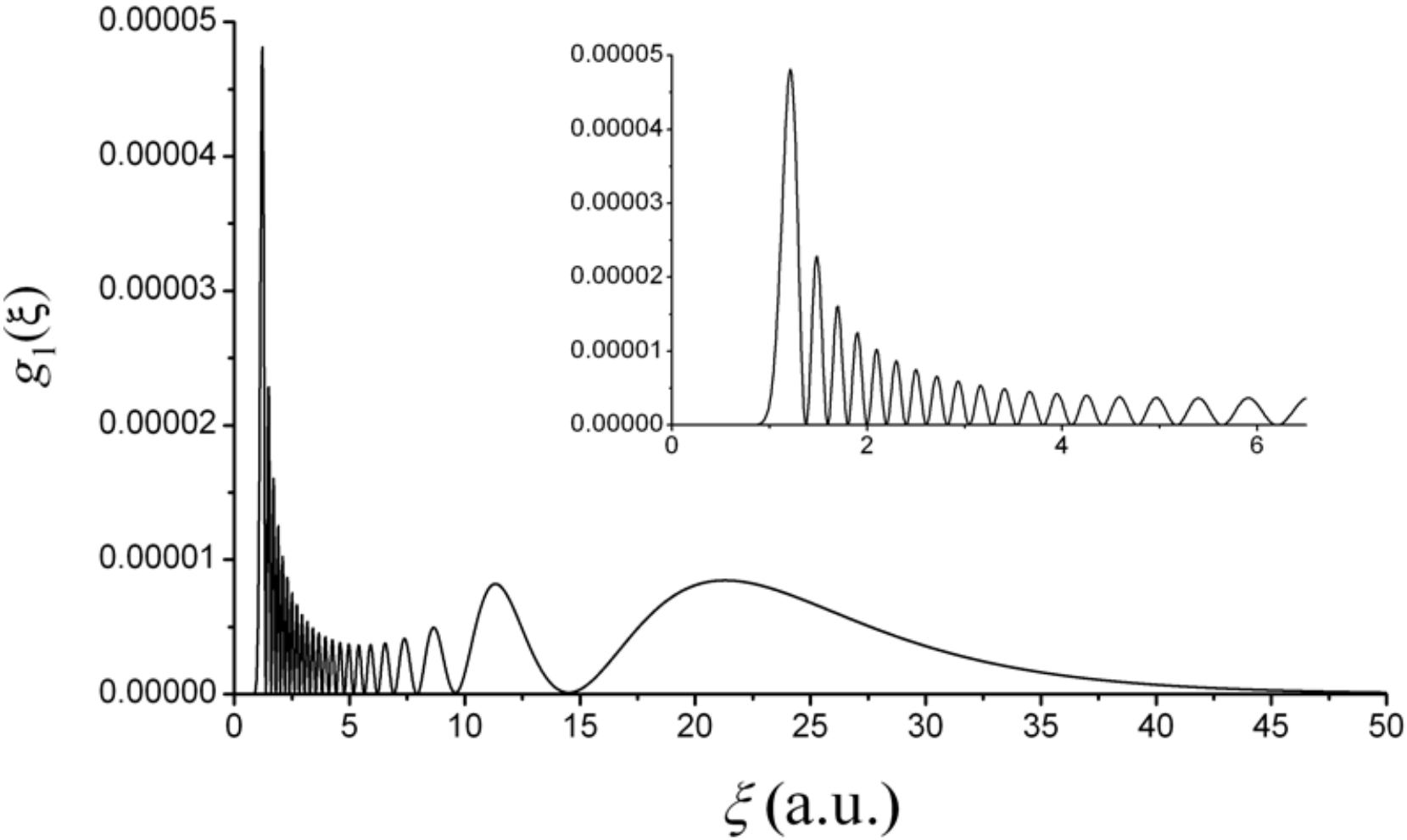
Transition	Isotope	Basis size	ΔE_{nr}	$\Delta E_{\mathrm{nr+rel}}$	$\Delta E_{\mathrm{nr+rel+QED}}$
$4s \rightarrow 3s$	^{11}B	12000	14968.254	14970.751	14970.429
	^{11}B	13000	14968.245	14970.740	14970.418
	^{11}B	14000	14968.239	14970.734	14970.412
	^{11}B	Exp. data[a]			14970.561(27)
$5s \rightarrow 3s$	^{11}B	12000	20103.087	20107.245	20106.662
	^{11}B	13000	20103.054	20107.210	20106.627
	^{11}B	14000	20103.028	20107.185	20106.602
	^{11}B	Exp. data[a]			20106.747(20)
$6s \rightarrow 3s$	^{11}B	12000	22434.630	22444.369	22442.814
	^{11}B	13000	22434.513	22444.254	22442.699
	^{11}B	14000	22434.424	22444.166	22442.611
	^{11}B	Exp. data[a]			22442.50(14)

[a] A. E. Kramida and A. N. Ryabtsev, Phys. Scr. 76, 544 (2007)

- Ultimate theoretical spectroscopy of small molecules
- Utilizing the machinery developed for atomic systems



BO potential energy curve of H_2^+



Deuteron–proton correlation function for $v = 22$ state of HD^+.

$$g(\boldsymbol{\xi}) \equiv \langle \psi \, | \delta(\mathbf{r}_{p-d} - \boldsymbol{\xi}) | \, \psi \rangle \, .$$

Explicitly correlated Gaussians with premultipliers:

$$\phi_k = r_1^m \exp\left[-\mathbf{r}'(A_k \otimes I_3)\,\mathbf{r}\right].$$

$$\phi_k = r_1^{m_1} r_2^{m_2} r_{12}^{m_{12}} \exp\left[-\mathbf{r}'(A_k \otimes I_3)\,\mathbf{r}\right].$$

Shifted Gaussians:

$$\phi_k = \exp\left[-(\mathbf{r}-\mathbf{s})'(A_k \otimes I_3)\,(\mathbf{r}-\mathbf{s})\right].$$

Complex Gaussians:

$$\begin{aligned}\phi_k &= \exp\left[-\mathbf{r}'(A_k \otimes I_3)\,\mathbf{r} - i\,\mathbf{r}'(B_k \otimes I_3)\,\mathbf{r}\right] \\ &= \exp\left[-\mathbf{r}'(C_k \otimes I_3)\,\mathbf{r}\right].\end{aligned}$$

A comparison of the total non-BO energies (in a.u.) of some selected rovibrational states of the HD^+ ion obtained with CECG basis and the basis of ECGs containing prefactors in the form of powers of the internuclear distance.

ν	Basis size and type	Energy
0	1300 CECG	-0.5978979686
	2000 ECG	-0.5978979685
	3000 ECG	-0.5978979686
	4000 ECG	-0.5978979686
1	1300 CECG	-0.5891818295
	2000 ECG	-0.5891818291
	3000 ECG	-0.5891818295
	4000 ECG	-0.5891818295
2	1300 CECG	-0.5809037000
	2000 ECG	-0.5809037001
	3000 ECG	-0.5809037002
	4000 ECG	-0.5809037002

ν	Basis size and type	Energy
7	1300 CECG	-0.5456859019
	2000 ECG	-0.5456859137
	3000 ECG	-0.5456859149
	4000 ECG	-0.5456859150
22	600 CECG	-0.4998538944
	800 CECG	-0.4998651297
	1000 CECG	-0.4998656097
	1000 ECG	-0.4998642516
	1500 ECG	-0.4998657469
	2000 ECG	-0.4998657692
	3000 ECG	-0.4998657766
	7000 ECG	-0.4998657783
	D atom	-0.4998638152

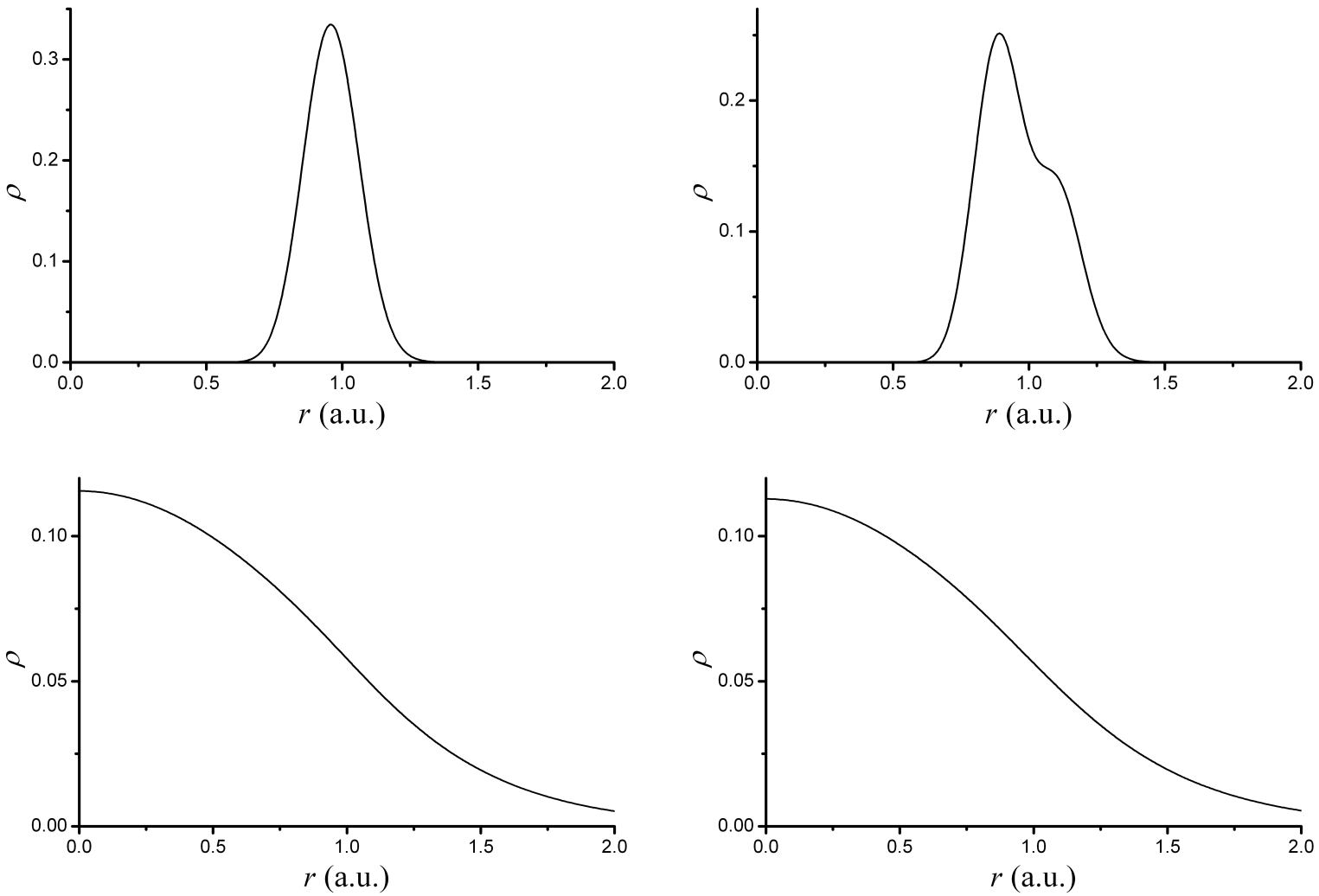
The ground state total non-BO nonrelativistic energy of of DH_2^+ computed with different number of complex Gaussian basis functions. All numbers are in a.u.

basis size	$E(v=0)$
200	−1.31745
400	−1.32136
600	−1.32299
800	−1.32355
1000	−1.32413
1200	−1.32440
1400, Shifted Gaussians[a]	−1.32270

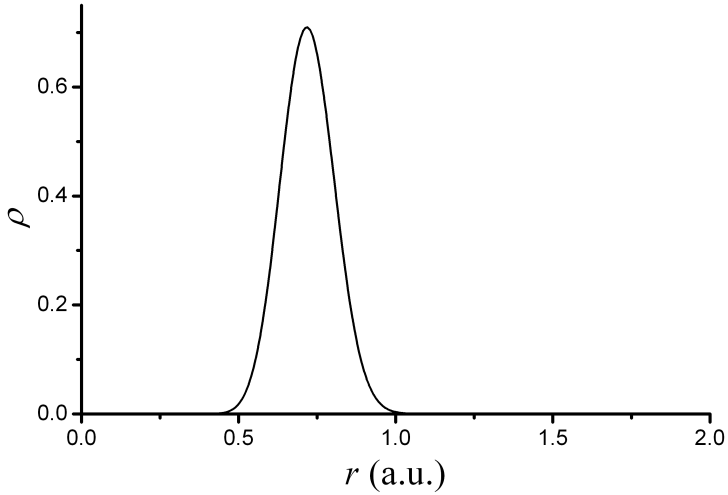
[a] M. Cafiero, and L. Adamowicz, J. Chem. Phys. **122**, 184305 (2005).

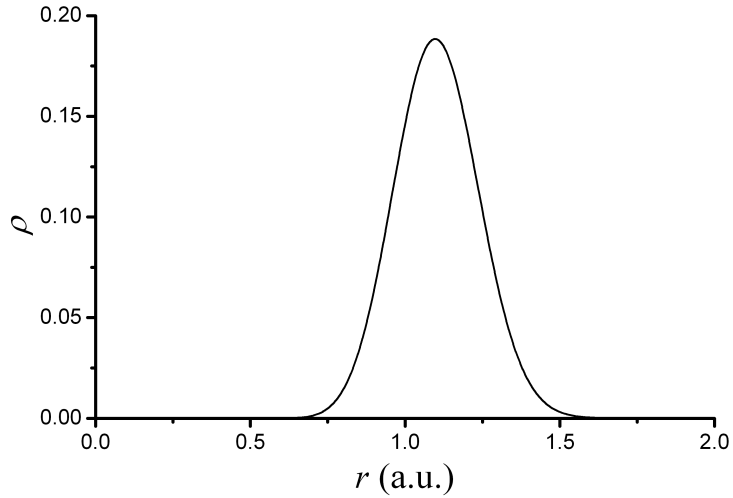
Expectation values of the internuclear distances for D_3^+ and DH_2^+ (in a.u.). computed using 800-tems basis sets for D_3^+ and 1200-term basis set for DH_2^+.

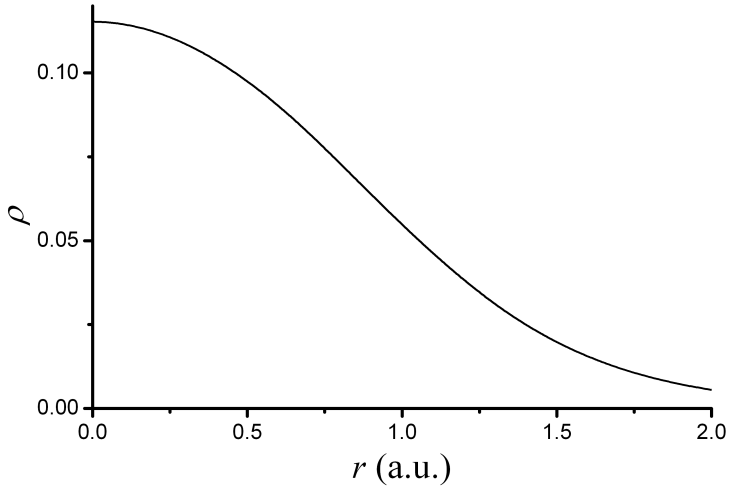
quantity	$D_3^+(v=0)$	$D_3^+(v=1)$	$DH_2^+(v=0)$
$\langle r_{d-d} \rangle$	1.7013	1.7416	
$\langle r_{d-p} \rangle$			1.7127
$\langle r_{p-p} \rangle$			1.7247
$\langle r_{d-e} \rangle$	1.6046	1.6316	1.6104
$\langle r_{p-e} \rangle$			1.6165
$\langle r_{e-e} \rangle$	2.0202	2.0508	2.0307
$\langle r_{d-d}^2 \rangle$	2.9246	3.0932	
$\langle r_{d-p}^2 \rangle$			2.9723
$\langle r_{p-p}^2 \rangle$			3.0195
$\langle r_{d-e}^2 \rangle$	3.1050	3.2234	3.1309
$\langle r_{p-e}^2 \rangle$			3.1547
$\langle r_{e-e}^2 \rangle$	4.7856	4.9423	4.8372



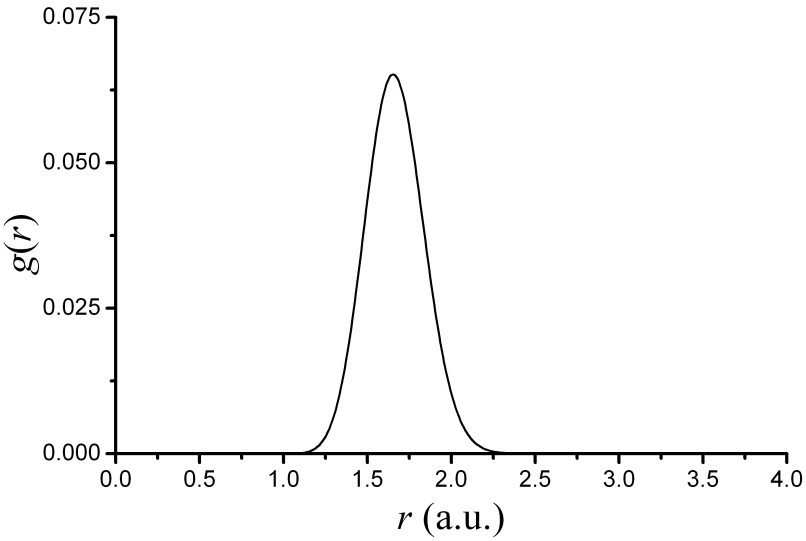
The deuteron (top row) and electron (bottom row) CMF-densities, $\rho_i(\boldsymbol{\xi}) \equiv \langle \psi \left| \delta(\mathbf{R}_i - \mathbf{r}_0 - \boldsymbol{\xi}) \right| \psi \rangle$, in the ground (left column) and first excited (right column) states of D_3^+.

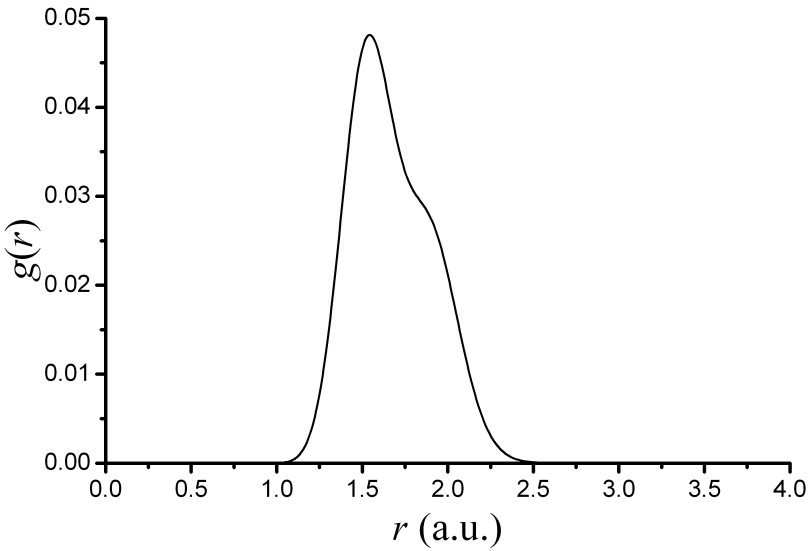






The deuteron (left), proton (right), and electron (bottom) CMF-densities in the ground state of DH_2^+.





Deuteron-deuteron correlation functions for $v = 0$ (left) and $v = 1$ (right) states of D_3^+.

- CECGs is an attractive option for non-Born–Oppenheimer calculations of small molecules
- Excellent results for HD^+
- Linear dependencies tend to cause serious problems for more sophisticated systems
- Treatment of relativistic/QED effects should be much easier in the framework of CECG
- Many useful things can be employed, e.g. expectation value identities

Acknowledgments

Collaborators:

- Keeper Sharkey, Martin Formanek, Nikita Kirnosov (University of Arizona)
- Kálmán Varga (Vanderbilt University)
- Monika Stanke (University of Toruń)

Former undergraduate students:

- Yerbolat Dauletyarov, Rustam Gatamov

This work has been supported by the Ministry of Education and Science of Kazakhstan