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# Molecular structure calculations: A unified quantum mechanical description of electrons and nuclei using explicitly correlated Gaussian functions and the global vector representation

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We elaborate on the theory for the variational solution of the Schrödinger equation of small atomic and molecular systems without relying on the Born–Oppenheimer paradigm. The all-particle Schrödinger equation is solved in a numerical procedure using the variational principle, Cartesian coordinates, parameterized explicitly correlated Gaussian functions with polynomial prefactors, and the global vector representation. As a result, non-relativistic energy levels and wave functions of few-particle systems can be obtained for various angular momentum, parity, and spin quantum numbers. A stochastic variational optimization of the basis function parameters facilitates the calculation of accurate energies and wave functions for the ground and some excited rotational-(vibrational-)electronic states of  $\text{H}_2^+$  and  $\text{H}_2$ , three bound states of the positronium molecule,  $\text{Ps}_2$ , and the ground and two excited states of the  $^7\text{Li}$  atom. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4731696>]

## I. INTRODUCTION

The clamped nuclei or Born–Oppenheimer (BO) approximation<sup>1–3</sup> is one of the central paradigms of present day theoretical and computational chemistry. This paper is devoted to a theoretical approach, which does not rely on this paradigm. A recent overview of such a pre-Born–Oppenheimer or “molecular structure” approach is given in Ref. 4, which also presents one of the central conceptual problems of molecular structure theory: the reconstruction of the classical molecular structure from a fully quantum mechanical description.<sup>4–19</sup> Numerical contributions to this question can be found in Refs. 20–29. In recent work,<sup>25,26</sup> we introduced radial and angular density functions to recognize elements of classical molecular structure in the all-particle quantum theory as strong correlation effects for the nuclei. Using these concepts the atomic-to-molecular transition was observed for a three-particle system by rescaling the relative mass of the particles in the calculations.<sup>25</sup>

In this work, we report on the development of a variational approach for the accurate calculation of energy levels and wave functions of few-particle systems with various angular momentum, parity, and spin quantum numbers. Methodological contributions to this field have a long history in the physicists’ community<sup>30–35</sup> and have found increasing interest in the molecular domain.<sup>36–38</sup> We can only note here that there are also efforts toward chemical and possible biochemical applications of a quantum electrons-nuclei theory.<sup>39–42</sup> Another interesting direction is a variational reduced-density matrix theory for electrons and protons.<sup>43</sup>

Our goal here is the accurate solution of the Schrödinger equation of few-particle systems. We describe electrons and atomic nuclei (or other particles) on equal footing, while focusing on the molecular domain. We are aiming at “spectroscopic accuracy.”<sup>44</sup> This is motivated by high-resolution measurements of the bonding energy of the  $\text{H}_2$  molecule<sup>45,46</sup> and post-Born–Oppenheimer calculations including relativistic and quantum-electrodynamic corrections<sup>47,48</sup> as well as by spectroscopic investigations of the  $\text{H}_3^+$  molecular ion.<sup>49–51</sup> Following the recent methodological developments in Ref. 37 and especially in Refs. 35, 52, and 53, we had to solve some technical issues to be able to use these ideas for our purposes.

The usage of explicitly correlated Gaussian functions considering the pioneering contributions<sup>54–56</sup> since the early work of Boys and Singer,<sup>57,58</sup> the inclusion of polynomial prefactors, and the global vector representation (GVR) (Refs. 35, 53, and 59) appear to be an appealing combination for the construction of a flexible basis set with the required spatial symmetry. This parameterization allows one to include polynomial prefactors in terms of more than one coordinate. However, it was noted in Refs. 60 and 61 that in the case of polynomial prefactors for several coordinates with large exponents instabilities might appear during the integral evaluation in a numerical procedure. Our preliminary tests indicated similar problems for a direct implementation of the formulae in Refs. 35 and 53. At the same time, small exponents in the polynomial prefactors were not sufficient for an efficient calculation of the energy levels of molecular systems. Thus, we decided to rearrange the original formulation<sup>35,53</sup> and make it applicable to molecular systems in practice. This would allow us the variational calculation of energy levels and wave function of molecules with not only zero, for example, Refs. 37, 62, and 63 but also non-zero (rotational or orbital) angular momentum quantum numbers within a pre-Born–Oppenheimer approach.

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As to the parameterization of the basis functions, a stochastic optimization of the parameters<sup>30,35,64–66</sup> can result in a flexible, on-the-fly adjustment of the basis set to various systems. We shall address the questions how to choose an “appropriate” random number generator for the stochastic optimization and whether this choice has an effect on the efficiency of the procedure.

Finally, for actual calculations, one can use laboratory-fixed (LF) or various translationally invariant Cartesian coordinates, e.g., Radau or Jacobi coordinate sets. Also in this context various questions arise: Which is the best choice? Does this choice have any effect on the convergence rate of the energy? We decided to stick to (laboratory-fixed or translationally invariant) Cartesian coordinates, which allows us to write the Hamiltonian in a simple form, in contrast to the common choice of curvilinear coordinates in BO rotational-vibrational calculations, which results in complicated kinetic energy operators (see, for example, Refs. 67–70).

In Sec. II, we summarize first the necessary theory, and then we describe our solutions to the technical issues raised above. In the paper, we indicate only the main steps of the integral evaluation and our choices made to restore the numerical stability in our calculations, while the lengthy integral formulae are collected in the supplementary material.<sup>71</sup> Based on the methodological details presented in Sec. II, a computer program was developed using the FORTRAN 90 programming language.

To demonstrate the applicability of this program, we report in Sec. III numerical results for rotational(-vibrational) energy levels corresponding to the ground and some electronically excited states of the  $\text{H}_2^+$  and  $\text{H}_2$  molecules; three bound states of the positronium molecule  $\text{Ps}_2$ , and the ground and two excited states of the  $^7\text{Li}$  atom. Finally, we investigate the transferability of the optimized basis function parameters and point out possible directions for future methodological developments.

## II. VARIATIONAL SOLUTION OF THE MANY-PARTICLE SCHRÖDINGER EQUATION

### A. Quantum Hamiltonian and the Pauli principle

The non-relativistic quantum Hamiltonian in Hartree atomic units and expressed in Cartesian coordinates in the LF,  $\mathbf{r}_i$  for  $i = 1, 2, \dots, n_p + 1$  particles, is

$$\hat{H} = \hat{T} + \hat{V} \quad (1)$$

with the kinetic and the potential energy terms

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

$$\hat{V} = \sum_{i=1}^{n_p+1} \sum_{j>i}^{n_p+1} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (3)$$

respectively, where the masses,  $m_i$ , and the electric charges,  $q_i$ , are properties associated to the point-like particles. The physically relevant eigenstates of this Hamiltonian satisfy the Pauli principle, i.e., conditions of the spin-statistics theorem

considering the bosonic or fermionic nature of the particles associated with some spin  $s_i$ .

Instead of re-expressing this Hamiltonian using translational, orientational, and internal coordinates, we use Cartesian coordinates and set up a trial wave function in a variational procedure as a linear combination of symmetry-adapted basis functions, which are angular momentum (total spatial angular momentum, i.e., angular momentum without the spins), parity, and spin eigenfunctions. As a result, the eigenvalues and eigenfunctions are obtained according to the quantum numbers of the non-relativistic theory.

Since we do not want to specify at the outset of the theoretical description the particle types, we simply use  $L$  for total spatial (rotational or orbital) angular momentum quantum number. For the notation of the total spin quantum number for particles  $a$ , we use the symbol  $S_a$ . At a later stage, when the particle types and the system are specified one can adapt the common notations in atomic and molecular spectroscopy (see for example the recommendations of the International Union of Pure and Applied Chemistry, Ref. 72):  $N$  for the total spatial angular momentum without the spins and  $S$  and  $I$  for the electronic and nuclear spin quantum numbers.

### B. Translationally invariant coordinates and Hamiltonian

In order to obtain a translationally invariant wave function,  $\Phi$ , for an  $(n_p + 1)$ -particle system there are two ways to proceed, see, for example, Ref. 20. (A) One can either parameterize the basis functions expressed in terms of LF Cartesian coordinates,  $\mathbf{r} \in \mathbb{R}^{3(n_p+1)}$ , and choose the parameters so that the overall momentum for the wave function is zero, i.e.,  $\hat{\mathbf{P}}_{\text{total}} \Phi = 0$ ; or (B) one can transform the LF Cartesian coordinates to some translationally invariant (TI) set of Cartesian coordinates,  $\mathbf{x} \in \mathbb{R}^{3n_p}$  plus the coordinates of the center of mass (CM),  $\mathbf{R}_{\text{CM}} \in \mathbb{R}^3$  by a linear transformation

$$\begin{pmatrix} \mathbf{x} \\ \mathbf{R}_{\text{CM}} \end{pmatrix} = (\mathbf{U} \otimes \mathbf{I}_3) \mathbf{r} \quad \text{and} \quad \mathbf{r} = (\mathbf{U}^{-1} \otimes \mathbf{I}_3) \begin{pmatrix} \mathbf{x} \\ \mathbf{R}_{\text{CM}} \end{pmatrix} \quad (4)$$

with  $\mathbf{U} \in \mathbb{R}^{(n_p+1) \times (n_p+1)}$ . The coordinates  $\mathbf{x}$  are translationally invariant<sup>73</sup> if

$$\sum_{j=1}^{n_p+1} U_{ij} = 0, \quad i = 1, 2, \dots, n_p \quad (5)$$

and

$$U_{n_p+1,j} = m_j / m_{\text{tot}}, \quad j = 1, 2, \dots, n_p + 1 \quad (6)$$

with  $m_{\text{tot}} = \sum_{j=1}^{n_p+1} m_j$ .

Then, the Hamiltonian is transformed accordingly and after subtracting the kinetic energy of the translational motion of the center of mass,  $\hat{T}_{\text{CM}} = -1/(2m_{\text{tot}}) \Delta_{\mathbf{R}_{\text{CM}}}$ , we have

$$\begin{aligned} \hat{H}' = \hat{H} - \hat{T}_{\text{CM}} = & - \sum_{i=1}^{n_p} \sum_{j=1}^{n_p} M_{ij} \nabla_{x_i}^T \nabla_{x_j} \\ & + \sum_{i=1}^{n_p+1} \sum_{j>i}^{n_p+1} \frac{q_i q_j}{|(\mathbf{f}_{ij} \otimes \mathbf{I}_3)^T \mathbf{x}|} \end{aligned} \quad (7)$$

with  $\nabla_{x_i}^T = (\partial/\partial x_{i1}, \partial/\partial x_{i2}, \partial/\partial x_{i3})$ .  $\mathbf{I}_3 \in \mathbb{R}^{3 \times 3}$  is the unit matrix, the masses are contained in

$$M_{ij} = \sum_{k=1}^{n_p+1} U_{ik} U_{jk} / 2m_k, \quad (8)$$

and the  $k$ th element ( $k = 1, 2, \dots, n_p$ ) of  $f_{ij}$  is defined as

$$(f_{ij})_k = (\mathbf{U}^{-1})_{ik} - (\mathbf{U}^{-1})_{jk}. \quad (9)$$

We note that the total spatial angular momentum relative to the center of mass commutes with the translationally invariant Hamiltonian.<sup>20,73,74</sup> In this work, we make use of both the coordinates defined according to (A) and (B). However, we will always apply those that lead to a simpler formulation.

### C. Symmetry-adapted basis functions, parameterization

We apply basis functions constructed as (anti)symmetrized products of spin functions and spatial functions, which are angular momentum and parity eigenfunctions. Thus, the ansatz for some set of quantum numbers  $\lambda = (L, M_L, p)$  and  $\varsigma = (S_a, M_{S_a}, S_b, M_{S_b}, \dots)$  ( $a, b, \dots$  denote the particle type) is constructed as

$$\Phi^{[\lambda, \varsigma]} = \hat{\mathcal{A}}\{\phi^{[\lambda]} \chi^{[\varsigma]}\} \quad (10)$$

with the symmetrization and antisymmetrization operator

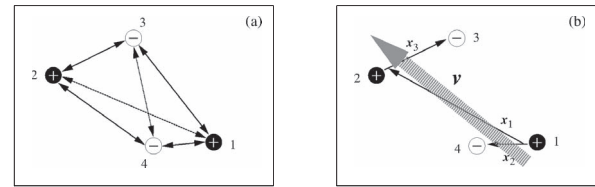
$$\hat{\mathcal{A}} = (N_{\text{perm}})^{-1/2} \sum_{p=1}^{N_{\text{perm}}} \varepsilon_p \hat{P}_p \quad (11)$$

for bosonic and fermionic-type particles, respectively.  $\hat{P}_p \in \mathcal{S}_{n_a} \otimes \mathcal{S}_{n_b} \otimes \dots$  is an operator permuting identical particles and  $\varepsilon_p = -1$  if  $\hat{P}_p$  represents an odd number of interchanges of fermions, otherwise  $\varepsilon_p = +1$ .  $N_{\text{perm}}$  is the number of all possible permutations.

#### 1. Spatial functions

Spatial functions with some  $\lambda = (L, M_L, p)$  can be constructed through the successive coupling of angular momenta of the subsystems within the partial wave decomposition (PWD) formalism. It was shown in Refs. 35, 53, and 59 that there is an alternative and equivalent route, named the global vector representation (GVR), which relies on a linear combination of several basis functions with some global vectors whose orientation as well as the linear combination coefficients are optimized variationally. The resulting function is an angular momentum and parity eigenfunction, while the partial wave contributions, which do not correspond to any “exact” quantum number, are optimized in the variational procedure. In our work, the main advantage of the GVR over the PWD is its simple and direct applicability for many-particle systems with an arbitrary angular momentum quantum number.

Thus, the spatial basis functions (Figure 1) are explicitly correlated Gaussian functions in the form recommended in Refs. 35, 53, and 59, which describe the particle-particle correlation by including products of Gaussian geminals, polynomial prefactors, and an angular function, which is a spherical



Particle-particle interactions,  $\alpha_{ij}$

Angular distribution,  $u_i$

FIG. 1. Visual representation of the inter-particle and the angular parts of the basis functions for a four-particle system: (a) *Particle-particle interactions*: particle-particle displacement vectors and the corresponding geminal exponents,  $\alpha_{ij}$ , are used to describe the inter-particle correlation; (b) *Angular distribution*: “atoms-in-molecule”-type coordinates are used in this example to express the global vector  $\mathbf{v} = u_1 \mathbf{x}_1 + u_2 \mathbf{x}_2 + u_3 \mathbf{x}_3$  with the “inter-atomic” coordinate,  $\mathbf{x}_1 = m_+ / (m_+ - m_-) (\mathbf{r}_2 - \mathbf{r}_1) + m_- / (m_+ - m_-) (\mathbf{r}_3 - \mathbf{r}_4)$  and the “intra-atomic” coordinates,  $\mathbf{x}_2 = \mathbf{r}_4 - \mathbf{r}_1$  and  $\mathbf{x}_3 = \mathbf{r}_3 - \mathbf{r}_2$ . Note that the (anti)symmetrization of the product of the spatial and spin functions guarantees that identical particles enter the description equivalently.

harmonic function of  $L$ th order and  $M_L$ th degree and depends on the orientation of the global vector  $\mathbf{v}$ ,

$$\phi^{[\lambda]}(\mathbf{r}; \boldsymbol{\alpha}, \mathbf{u}, K) = |\mathbf{v}|^{2K+L} Y_{LM_L}(\hat{\mathbf{v}}) \times \exp \left( -\frac{1}{2} \sum_{i=1}^{n_p+1} \sum_{j>i}^{n_p+1} \alpha_{ij} (\mathbf{r}_i - \mathbf{r}_j)^2 \right), \quad (12)$$

where  $\hat{\mathbf{v}}$  is a collective label for the spherical angles characterizing the orientation of the unit vector  $\mathbf{v}/|\mathbf{v}|$  with

$$\mathbf{v} = \sum_{i=1}^{n_p+1} \mathbf{u}_i^{(0)} \mathbf{r}_i = (\mathbf{u}^{(0)} \otimes \mathbf{I}_3)^T \mathbf{r} \quad (13)$$

and  $(\mathbf{u}^{(0)})^T = (\mathbf{u}_1^{(0)}, \mathbf{u}_2^{(0)}, \dots, \mathbf{u}_{n_p+1}^{(0)})$ . As to the parameterization corresponding to LF Cartesian coordinates (approach (A)), the  $\sum_{i=1}^{n_p+1} \mathbf{u}_i^{(0)} = 0$  condition is introduced to guarantee zero overall momentum for the basis function.

#### 2. Integral transformation, generator coordinates

During the evaluation of the matrix elements not the original form of the basis functions given in Eq. (12) is used, but it is generated by the integral transformation<sup>53</sup>

$$\phi^{[\lambda]}(\mathbf{r}; \mathcal{A}, \mathbf{u}, K) = \frac{1}{\mathcal{B}_{KLp}} \int d\hat{\mathbf{e}} \eta_{LM_Lp}(\hat{\mathbf{e}}) \times \{ \hat{\mathcal{D}}_a^{(2K+L)} g(\mathbf{r}; \mathcal{A}, s(\mathbf{a}, \mathbf{u}, \mathbf{e})) \}_{a_i=0, |e_i|=1} \quad (14)$$

with the generating function

$$g(\mathbf{r}; \mathcal{A}, s) = \exp \left( -\frac{1}{2} \mathbf{r}^T (\mathcal{A} \otimes \mathbf{I}_3) \mathbf{r} + s^T \mathbf{r} \right), \quad (15)$$

where  $s \in \mathbb{R}^{3(n_p+1)}$  is also called the generator coordinate and the definition of the symbols are collected in Table I for any  $L, M_L$ , and  $p$  values including both the “natural-parity,”  $p = (-1)^L$ , and the “unnatural-parity,”  $p = (-1)^{L+1}$ , cases.

In this work, we present results obtained using the basis functions with label “A” of Table I, i.e., states with arbitrary angular momentum quantum numbers,  $L$ , and “natural parity,”  $p = (-1)^L$ . We have obtained preliminary results with



TABLE I. Explanation of the notation used in the general definition of basis functions, Eq. (14), with angular momentum  $L$ ,  $M_L$ , and parity  $p$ .

$L$	$p$	$\mathcal{B}_{KLp}^a$	$\hat{e}^b$	$\eta_{LM_Lp}(\hat{e})^{b,c}$	$s$	$\hat{\mathcal{D}}_a^{(\kappa)d}$	Label
$>0$	$(-1)^L$	$B_{KL}$	$\hat{e}_1$	$Y_{LM_L}(\hat{e}_1)$	$a_1 \mathbf{u}_1 \otimes \mathbf{e}_1$	$\partial_{a_1}^\kappa$	A
$>1$	$(-1)^{L+1}$	$B_{01} B_{KL}$	$(\hat{e}_1, \hat{e}_2)$	$[Y_L(\hat{e}_1) Y_1(\hat{e}_2)]_{LM_L}$	$\sum_{i=1}^2 a_i \mathbf{u}_i \otimes \mathbf{e}_i$	$\partial_{a_1}^\kappa \partial_{a_2}$	B
$=0$	$-1$	$B_{01}^2 B_{KL}$	$(\hat{e}_1, \hat{e}_2, \hat{e}_3)$	$[Y_1(\hat{e}_1) Y_1(\hat{e}_2)]_1 Y_1(\hat{e}_3)_{00}$	$\sum_{i=1}^3 a_i \mathbf{u}_i \otimes \mathbf{e}_i$	$\partial_{a_1}^\kappa \partial_{a_2} \partial_{a_3}$	C

<sup>a</sup> $B_{KL} = 4\pi(2K+L)!(K+L+1)!2^{L+1}/[K!(2K+2L+2)!]$  with  $K, L \in \mathbb{N}_0$ .

<sup>b</sup> $\hat{e}_i$  is the collective label for the spherical angles characterizing the orientation of the unit vector  $\mathbf{e}_i$ .

<sup>c</sup> $[Y_{l_1} Y_{l_2}]_{lm_l}$  denotes the coupling of the  $l_1$ th and  $l_2$ th spherical harmonics to the  $l$ th order and  $m_l$ th degree spherical harmonic function.

<sup>d</sup> $\kappa = 2K+L$  and the shorthand notation  $\partial_{a_i}^\kappa = \partial^k / \partial a_i^k$  are introduced.

functions of label “B”, i.e., “unnatural-parity” basis functions with  $p = (-1)^{L+1}$  for  $L > 0$ , but they are not discussed in the present work.

The generating function  $g(\mathbf{r}; \mathcal{A}, s)$  equals (within a constant factor) an explicitly correlated Gaussian function with shifted origin,  $\mathcal{R} \in \mathbb{R}^{3(n_p+1)}$  (in short, “floating geminal”) according to

$$\begin{aligned}
 f(\mathbf{r}; \mathcal{A}, \mathcal{R}) &= \exp\left(-\frac{1}{2}(\mathbf{r} - \mathcal{R})^T (\mathcal{A} \otimes \mathbf{I}_3) (\mathbf{r} - \mathcal{R})\right) \\
 &= \exp\left(-\frac{1}{2}\mathcal{R}^T (\mathcal{A} \otimes \mathbf{I}_3) \mathcal{R}\right) \\
 &\quad \times \exp\left(-\frac{1}{2}\mathbf{r}^T (\mathcal{A} \otimes \mathbf{I}_3) \mathbf{r} + \mathcal{R}^T (\mathcal{A} \otimes \mathbf{I}_3) \mathbf{r}\right),
 \end{aligned} \tag{16}$$

and thus by choosing  $\mathcal{R} = (\mathcal{A}^{-1} \otimes \mathbf{I}_3)s$  so that  $\mathcal{R}^T = s^T (\mathcal{A}^{-1} \otimes \mathbf{I}_3)$  ( $\mathcal{A}$  is symmetric and non-singular), we obtain

$$f(\mathbf{r}; \mathcal{A}, (\mathcal{A}^{-1} \otimes \mathbf{I}_3)s) = \exp\left(-\frac{1}{2}s^T (\mathcal{A}^{-1} \otimes \mathbf{I}_3)s\right) g(\mathbf{r}; \mathcal{A}, s). \tag{17}$$

The functions  $f$  and  $g$  with appropriate exponents  $\mathcal{A}$  describe well particles localized near  $\mathcal{R}$ , which is different from the origin. However, for such an  $\mathcal{R} \neq 0$  vector, they are not parity and angular momentum eigenfunctions. It is the integral transformation of Eq. (14), which restores the space rotation-inversion symmetry of an isolated system for  $g$ .

We note that this approach can be considered as a special application of the more general “generator coordinate method” introduced by Hill and Wheeler in 1953 (Ref. 75) with one of first applications in chemistry during the late 1970s by Lathouwers, van Leuven, and co-workers.<sup>76,77</sup> We also note here that the ansatz introduced in Eq. (12) shows similarities with the “Hagedorn-type” wave packets<sup>78</sup> used, for example, in Ref. 79. Of course, the space rotation-inversion symmetry for floating geminals could be restored numerically in a variational procedure, which was pursued by Adamowicz and Cafiero for  $L = 0$ , for example, in Ref. 22. It would also be interesting to consider this numerical reconstruction of the spatial symmetry for higher  $L$  values, but for the present work we stick to the analytic expressions and employ Eq. (14).

### 3. Linear transformation of the coordinates, channels

The LF Cartesian coordinates,  $\mathbf{r}$ , and various sets of translationally invariant Cartesian coordinates, say  $\mathbf{x}$  or  $\mathbf{y}$ , together with the coordinates of the center of mass,  $\mathbf{R}_{\text{CM}}$ , are related by simple linear transformations

$$\begin{aligned}
 \begin{pmatrix} \mathbf{x} \\ \mathbf{R}_{\text{CM}} \end{pmatrix} &= (\mathbf{U} \otimes \mathbf{I}_3) \mathbf{r} \text{ and } \mathbf{r} = (\mathbf{U}^{-1} \otimes \mathbf{I}_3) \begin{pmatrix} \mathbf{x} \\ \mathbf{R}_{\text{CM}} \end{pmatrix} \\
 \begin{pmatrix} \mathbf{y} \\ \mathbf{R}_{\text{CM}} \end{pmatrix} &= (\mathbf{V} \otimes \mathbf{I}_3) \mathbf{r} \text{ and } \mathbf{r} = (\mathbf{V}^{-1} \otimes \mathbf{I}_3) \begin{pmatrix} \mathbf{y} \\ \mathbf{R}_{\text{CM}} \end{pmatrix}
 \end{aligned} \tag{18}$$

so that

$$\begin{pmatrix} \mathbf{y} \\ \mathbf{R}_{\text{CM}} \end{pmatrix} = (\mathbf{V} \mathbf{U}^{-1} \otimes \mathbf{I}_3) \begin{pmatrix} \mathbf{x} \\ \mathbf{R}_{\text{CM}} \end{pmatrix}$$

and

$$\begin{pmatrix} \mathbf{x} \\ \mathbf{R}_{\text{CM}} \end{pmatrix} = (\mathbf{U} \mathbf{V}^{-1} \otimes \mathbf{I}_3) \begin{pmatrix} \mathbf{y} \\ \mathbf{R}_{\text{CM}} \end{pmatrix} \tag{19}$$

hold. We thus can easily switch from one set of coordinates to another.

By switching between the coordinates, the mathematical form of the spatial functions remains unchanged and only the parameters have to be transformed. This “re-parameterization” of the basis functions by changing the coordinate representation reads

$$\begin{aligned}
 \phi^{[\lambda]} &= |\mathbf{v}|^{2K+L} Y_{LM_L}(\hat{\mathbf{v}}) \exp\left(-\frac{1}{2}\mathbf{r}^T (\mathcal{A}^{(0)} \otimes \mathbf{I}_3) \mathbf{r}\right) \\
 &= |\mathbf{v}|^{2K+L} Y_{LM_L}(\hat{\mathbf{v}}) \exp\left(-\frac{1}{2}\mathbf{x}^T (\mathcal{A}^{(x)} \otimes \mathbf{I}_3) \mathbf{x}\right) \\
 &= |\mathbf{v}|^{2K+L} Y_{LM_L}(\hat{\mathbf{v}}) \exp\left(-\frac{1}{2}\mathbf{y}^T (\mathcal{A}^{(y)} \otimes \mathbf{I}_3) \mathbf{y}\right),
 \end{aligned} \tag{20}$$

where the exponents

$$(\mathcal{A}^{(0)})_{ij} = -\alpha_{ij}(1 - \delta_{ij}) + \left( \sum_{k=1, k \neq i}^{n_p+1} \alpha_{ik} \right) \delta_{ij} + c_A \frac{m_i}{m_{\text{tot}}} \frac{m_j}{m_{\text{tot}}} \tag{21}$$

are transformed according to

$$\mathcal{A}^{(x)} = \mathbf{U}^{-T} \mathcal{A}^{(0)} \mathbf{U}^{-1} \Leftrightarrow \mathcal{A}^{(0)} = \mathbf{U}^T \mathcal{A}^{(x)} \mathbf{U}$$

and

$$\mathcal{A}^{(y)} = \mathbf{V}^{-T} \mathcal{A}^{(0)} \mathbf{V}^{-1} \Leftrightarrow \mathcal{A}^{(0)} = \mathbf{V}^T \mathcal{A}^{(y)} \mathbf{V}, \tag{22}$$

which also yields the relations

$$\mathcal{A}^{(y)} = (\mathbf{U}\mathbf{V}^{-1})^T \mathcal{A}^{(x)} \mathbf{U}\mathbf{V}^{-1} \quad (23)$$

and

$$\mathcal{A}^{(x)} = (\mathbf{V}\mathbf{U}^{-1})^T \mathcal{A}^{(y)} \mathbf{V}\mathbf{U}^{-1}. \quad (24)$$

Note that

$$\mathcal{A}^{(x)} = \begin{pmatrix} \mathbf{A}^{(x)} & \mathbf{0} \\ \mathbf{0} & c_A \end{pmatrix} \quad \text{and} \quad \mathcal{A}^{(y)} = \begin{pmatrix} \mathbf{A}^{(y)} & \mathbf{0} \\ \mathbf{0} & c_A \end{pmatrix}. \quad (25)$$

Similarly, the global vector can be written as

$$\mathbf{v} = (\mathbf{u}^{(0)} \otimes \mathbf{I}_3)^T \mathbf{r} = (\mathbf{u}^{(x)} \otimes \mathbf{I}_3)^T \mathbf{x} = (\mathbf{u}^{(y)} \otimes \mathbf{I}_3)^T \mathbf{y}, \quad (26)$$

where  $\mathbf{u}^{(0)}$ ,  $\mathbf{u}^{(x)}$ ,  $\mathbf{u}^{(y)}$  obey the transformations  $\mathbf{u}^{(x)} = \mathbf{U}^{-T} \mathbf{u}^{(0)}$ ,  $\mathbf{u}^{(0)} = \mathbf{U}^T \mathbf{u}^{(x)}$ ,  $\mathbf{u}^{(y)} = \mathbf{V}^{-T} \mathbf{u}^{(0)}$ ,  $\mathbf{u}^{(0)} = \mathbf{V}^T \mathbf{u}^{(y)}$ ,  $\mathbf{u}^{(x)} = (\mathbf{U}\mathbf{V}^{-1})^T \mathbf{u}^{(y)}$ , and  $\mathbf{u}^{(y)} = (\mathbf{V}\mathbf{U}^{-1})^T \mathbf{u}^{(x)}$ . Note also that

$$\mathbf{u}^{(x)} = \begin{pmatrix} u^{(x)} \\ c_u \end{pmatrix} \quad \text{and} \quad \mathbf{u}^{(y)} = \begin{pmatrix} u^{(y)} \\ c_u \end{pmatrix} \quad (27)$$

and the zero overall momentum of the basis function in the LF Cartesian representation is guaranteed if  $c_u = 0$ . The condition  $c_u = 0$  is equivalent to the requirement  $\sum_{i=1}^{n_p+1} \mathbf{u}_i^{(0)} = c_u = 0$  according to the properties of the transformation matrix, Eq. (6).

It is convenient to consider various coordinates for the calculations, for at least two reasons. First, the evaluation of the matrix elements can be simplified using a certain type of coordinates. Of course, the Jacobian of the coordinate transformation (here a constant) must be included in the volume element expressed in terms of the transformed coordinates (see Eq. (26) of Ref. 26). Second, different coordinates can represent efficiently different correlations (Figure 2), and thus the parameterization of the wave function expressed in terms of one set of coordinates can be more convenient than in terms of another set of coordinates. Additionally, the action of a permutation operation on the spatial coordinates is equivalent to a linear transformation of the Cartesian coordinates, and thus, its effect on the spatial functions can be accounted for by the transformation of the parameters.

Finally, we note here that since  $\mathbf{A}$  is real symmetric, it is always possible to find some set of translationally invariant coordinates, which corresponds to a diagonal exponent matrix,  $\mathbf{A}'$ , and thus an effective “one-particle” (pseudo-particle) basis function. As the wave function is written as a linear combinations of the basis functions with different exponent matrices, each of these exponent matrices is diagonal in some set of coordinates (“coordinate channels”), and thus the wave function can be written as a linear combination of this multiple-channel basis set.

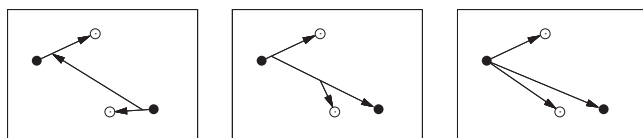


FIG. 2. Examples for translationally invariant Cartesian coordinates for four particles. Every choice can describe different correlations efficiently.

#### 4. Spin functions

In this work, we consider systems in which only the coupling of spin-1/2 particles occur. A spin-1/2 particle can have  $\alpha$  and  $\beta$  spin functions,  $\sigma_{\frac{1}{2}, \frac{1}{2}}(1) = |\uparrow\rangle_\sigma$  and  $\sigma_{\frac{1}{2}, -\frac{1}{2}}(1) = |\downarrow\rangle_\sigma$  corresponding to  $(s_\alpha, m_{s_\alpha}) = (\frac{1}{2}, \frac{1}{2})$  and  $(s_\beta, m_{s_\beta}) = (\frac{1}{2}, -\frac{1}{2})$ , respectively (the subscript  $\sigma$  refers to the spin degree(s) of freedom). For  $n$  identical particles, products of one-particle spin functions (“elementary” spin functions or uncoupled basis representation) are coupled to the many-particle spin function,  $\Sigma_{S, M_S}(1, \dots, n)$ , with the total spin quantum numbers  $S$  and  $M_S$ .

The  $\alpha$  and  $\beta$  projections are distributed between the  $n$  particles according to  $n = n_\alpha + n_\beta$  and  $M_S = m_{s_\alpha} n_\alpha + m_{s_\beta} n_\beta$ . Thus, each  $n$ -particle uncoupled basis function,  $\sigma_{\frac{1}{2}, m_{s_1}}(1) \dots \sigma_{\frac{1}{2}, m_{s_n}}(n)$ , which contribute to the  $n$ -particle total spin eigenfunction  $\Sigma_{S, M_S}(1, \dots, n)$ , must contain  $n_\alpha = n/2 + M_S$  and  $n_\beta = n/2 - M_S$  one-particle spin functions,  $\sigma_{\frac{1}{2}, m_{s_i}}(i)$ , which can be written down in all possible permutations, resulting in a total of  $N_s = \binom{n}{n_\alpha} = \binom{n}{n_\beta}$  uncoupled  $n$ -particle basis functions. Then,  $\Sigma_{S, M_S}(1, \dots, n)$  is expressed as a linear combination of the uncoupled basis functions using the Clebsch–Gordan expansion coefficients,  $\langle j_1, m_{j_1}, j_2, m_{j_2} | J, M_J \rangle$ , and the requirement that  $\Sigma_{S, M_S}(1, \dots, n)$  is normalized.

In the present work, we consider only systems with two and three identical spin-1/2 particles, and the spin functions corresponding to the calculated states are constructed as follows (the construction of any other spin function of systems with few spin-1/2 particles can be done similarly).

For two spin-1/2 particles, we use here the  $\Sigma_{0,0}(1, 2)$  (singlet) and the  $\Sigma_{1,0}(1, 2)$  (a triplet) spin functions. Both spin functions have well-known forms, which we present here to introduce notation needed later. For both  $\Sigma_{0,0}(1, 2)$  and  $\Sigma_{1,0}(1, 2)$  holds  $M_S = 0$ , and thus  $n_\alpha = n_\beta = 1$ . The number of uncoupled basis functions is  $N_s = \binom{n}{n_\alpha} = \binom{n}{n_\beta} = 2$ . Then, the total spin function can be obtained as

$$\begin{aligned} \Sigma_{0,0}(1, 2) &= [\sigma_{\frac{1}{2}}(1)\sigma_{\frac{1}{2}}(2)]_{0,0} \\ &= \langle \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}, -\tfrac{1}{2} | 0, 0 \rangle \sigma_{\frac{1}{2}, \frac{1}{2}}(1)\sigma_{\frac{1}{2}, -\frac{1}{2}}(2) \\ &\quad + \langle \tfrac{1}{2}, -\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2} | 0, 0 \rangle \sigma_{\frac{1}{2}, -\frac{1}{2}}(1)\sigma_{\frac{1}{2}, \frac{1}{2}}(2) \\ &= \frac{1}{\sqrt{2}} \sigma_{\frac{1}{2}, \frac{1}{2}}(1)\sigma_{\frac{1}{2}, -\frac{1}{2}}(2) - \frac{1}{\sqrt{2}} \sigma_{\frac{1}{2}, -\frac{1}{2}}(1)\sigma_{\frac{1}{2}, \frac{1}{2}}(2) \\ &= \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle), \end{aligned} \quad (28)$$

where  $[\dots]_{jm_j}$  refers to the angular momentum coupling. Similarly, we obtain the triplet spin function as

$$\begin{aligned} \Sigma_{1,0}(1, 2) &= [\sigma_{\frac{1}{2}}(1)\sigma_{\frac{1}{2}}(2)]_{1,0} \\ &= \langle \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}, -\tfrac{1}{2} | 1, 0 \rangle \sigma_{\frac{1}{2}, \frac{1}{2}}(1)\sigma_{\frac{1}{2}, -\frac{1}{2}}(2) \\ &\quad + \langle \tfrac{1}{2}, -\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2} | 1, 0 \rangle \sigma_{\frac{1}{2}, -\frac{1}{2}}(1)\sigma_{\frac{1}{2}, \frac{1}{2}}(2) \\ &= \frac{1}{\sqrt{2}} \sigma_{\frac{1}{2}, \frac{1}{2}}(1)\sigma_{\frac{1}{2}, -\frac{1}{2}}(2) + \frac{1}{\sqrt{2}} \sigma_{\frac{1}{2}, -\frac{1}{2}}(1)\sigma_{\frac{1}{2}, \frac{1}{2}}(2) \\ &= \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle). \end{aligned} \quad (29)$$

For three spin-1/2 particles, the  $\Sigma_{\frac{1}{2},\frac{1}{2}}(1, 2, 3)$  (a doublet) spin function has  $M_S = 1/2$ , and thus  $n_\alpha = 2$  and  $n_\beta = 1$  with  $N_s = \binom{n}{n_\alpha} = \binom{n}{n_\beta} = 3$  uncoupled basis functions. Then, the total spin function expressed in terms of the uncoupled spin functions can be obtained by evaluating

$$\Sigma_{\frac{1}{2},\frac{1}{2}}(1, 2, 3) = c_1 \left[ \left[ \sigma_{\frac{1}{2}}(1) \sigma_{\frac{1}{2}}(2) \right]_1 \sigma_{\frac{1}{2}}(3) \right]_{\frac{1}{2},\frac{1}{2}} + c_2 \left[ \left[ \sigma_{\frac{1}{2}}(1) \sigma_{\frac{1}{2}}(2) \right]_0 \sigma_{\frac{1}{2}}(3) \right]_{\frac{1}{2},\frac{1}{2}}. \quad (30)$$

The normalization condition for  $\Sigma_{\frac{1}{2},\frac{1}{2}}(1, 2, 3)$  requires  $c_1^2 + c_2^2 = 1$ , which can be fulfilled by choosing  $c_1 = \sin \vartheta_1$  and  $c_2 = \cos \vartheta_1$  with  $\vartheta_1 \in [-\pi/2, \pi/2]$ , similar to Ref. 35. Then, we couple the one-particle spin functions, insert the corresponding Clebsch–Gordan coefficients, and obtain

$$\begin{aligned} \Sigma_{\frac{1}{2},\frac{1}{2}}(1, 2, 3) &= \sin \vartheta_1 \langle 1, 0, \frac{1}{2}, \frac{1}{2} | \frac{1}{2}, \frac{1}{2} \rangle \left[ \sigma_{\frac{1}{2}}(1) \sigma_{\frac{1}{2}}(2) \right]_{1,0} \sigma_{\frac{1}{2},\frac{1}{2}}(3) \\ &\quad + \sin \vartheta_1 \langle 1, 1, \frac{1}{2}, -\frac{1}{2} | \frac{1}{2}, \frac{1}{2} \rangle \left[ \sigma_{\frac{1}{2}}(1) \sigma_{\frac{1}{2}}(2) \right]_{1,1} \sigma_{\frac{1}{2},-\frac{1}{2}}(3) \\ &\quad + \cos \vartheta_1 \langle 0, 0, \frac{1}{2}, \frac{1}{2} | \frac{1}{2}, \frac{1}{2} \rangle \left[ \sigma_{\frac{1}{2}}(1) \sigma_{\frac{1}{2}}(2) \right]_{0,0} \sigma_{\frac{1}{2},\frac{1}{2}}(3) \\ &= \kappa_1(\vartheta_1) \sigma_{\frac{1}{2},\frac{1}{2}}(1) \sigma_{\frac{1}{2},-\frac{1}{2}}(2) \sigma_{\frac{1}{2},\frac{1}{2}}(3) \\ &\quad + \kappa_2(\vartheta_1) \sigma_{\frac{1}{2},\frac{1}{2}}(1) \sigma_{\frac{1}{2},\frac{1}{2}}(2) \sigma_{\frac{1}{2},-\frac{1}{2}}(3) \\ &\quad + \kappa_3(\vartheta_1) \sigma_{\frac{1}{2},-\frac{1}{2}}(1) \sigma_{\frac{1}{2},\frac{1}{2}}(2) \sigma_{\frac{1}{2},\frac{1}{2}}(3). \end{aligned} \quad (31)$$

Thus, in short the total spin function can be written as

$$\Sigma_{\frac{1}{2},\frac{1}{2}}(1, 2, 3) = \kappa_1(\vartheta_1) |\uparrow\downarrow\uparrow\rangle + \kappa_2(\vartheta_1) |\uparrow\uparrow\downarrow\rangle + \kappa_3(\vartheta_1) |\downarrow\uparrow\uparrow\rangle, \quad (32)$$

where we collected the linear combination coefficients in  $\kappa(\vartheta_1) = (\kappa_1(\vartheta_1), \kappa_2(\vartheta_1), \kappa_3(\vartheta_1))$

$$\kappa_1(\vartheta_1) = \frac{1}{\sqrt{2}} \cos \vartheta_1 - \frac{1}{\sqrt{6}} \sin \vartheta_1, \quad (33)$$

$$\kappa_2(\vartheta_1) = \sqrt{\frac{2}{3}} \sin \vartheta_1, \quad (34)$$

$$\kappa_3(\vartheta_1) = -\frac{1}{\sqrt{2}} \cos \vartheta_1 - \frac{1}{\sqrt{6}} \sin \vartheta_1. \quad (35)$$

If there are several types of identical particles,  $a, b, \dots$  in the system, the total spin function is constructed as

$$\chi_{S,M_S} = \Sigma_{S_a,M_{S_a}}(1, \dots, n_a) \Sigma_{S_b,M_{S_b}}(1, \dots, n_b) \dots \quad (36)$$

and here  $(S, M_S)$  is a collective index for  $(S_a, M_{S_a})$ ,  $(S_b, M_{S_b})$ ,  $\dots$ . Since the total spin function for any particle type  $a$ ,  $\Sigma_{S_a,M_{S_a}}(1, \dots, n_a)$ , can be written as a linear combination of uncoupled many-particle spin functions, the  $\chi_{S,M_S}$  function can also be written in a similar way, and thus for later convenience we introduce the shorthand notation

$$\chi_{S,M_S}(\boldsymbol{\vartheta}) = \sum_{n=1}^{N_s} \kappa_n(\boldsymbol{\vartheta}) |n\rangle_\sigma, \quad (37)$$

where  $|n\rangle_\sigma$  denotes the product of uncoupled many-particle spin functions for each particle type,  $N_s = N_{S_a} N_{S_b} \dots$ ,  $\sigma$  refers to the spin degrees of freedom, and  $\boldsymbol{\vartheta}$  contains the free parameters if there are several “partial waves.” The

value of  $\kappa_n(\boldsymbol{\vartheta})$  is determined by the normalization condition, the Clebsch–Gordan coefficients, and the angular momentum coupling procedure carried out for each particle types similar to Eqs. (28)–(35).

## 5. Permutation of identical particles

For the (anti)symmetrization of the product of the spatial and the spin functions, Eq. (10), we have to evaluate the effect of a permutation operator on this product by acting on both the spatial and the spin “coordinates”

$$\begin{aligned} \hat{P}_p \{ \phi^{[\lambda]} \chi^{[\zeta]} \} &= \{ \hat{P}_p \phi^{[\lambda]}(\mathbf{r}) \} \{ \hat{P}_p \chi^{[\zeta]} \} \\ &= \phi^{[\lambda]}(\hat{P}_p^{-1} \mathbf{r}) \sum_{n=1}^{N_s} \kappa_n(\boldsymbol{\vartheta}) \hat{P}_p |n\rangle_\sigma. \end{aligned} \quad (38)$$

To proceed, we construct the matrix representation of  $\hat{P}_p$  for both the elementary (uncoupled) spin functions,  $\mathbf{P}_p^s \in \mathbb{R}^{N_s \times N_s}$ , and for the LF Cartesian coordinates,  $\mathbf{P}_p^r \in \mathbb{R}^{(n_p+1) \times (n_p+1)}$  with

$$\hat{P}_p \mathbf{r} = (\mathbf{P}_p^r \otimes \mathbf{I}_3) \mathbf{r}. \quad (39)$$

Since the effect of  $\hat{P}_p$  is a simple permutation for both the elementary spin functions and the LF Cartesian coordinates, the corresponding matrices contain “0”s except for a single “1” element in each row and column. Then, we can write

$$\begin{aligned} \hat{P}_p \{ \phi^{[\lambda]} \chi^{[\zeta]} \} &= \phi^{[\lambda]}((\mathbf{P}_p^r \otimes \mathbf{I}_3)^{-1} \mathbf{r}; \mathbf{u}^{(0)}, \mathcal{A}^{(0)}) \\ &\quad \times \sum_{n=1}^{N_s} ((\mathbf{P}_p^s)^T \kappa(\boldsymbol{\vartheta}))_n |n\rangle_\sigma \\ &= \phi^{[\lambda]}(\mathbf{r}; \mathbf{u}_p^{(0)}, \mathcal{A}_p^{(0)}) \sum_{n=1}^{N_s} (\tilde{\kappa}_p(\boldsymbol{\vartheta}))_n |n\rangle_\sigma, \end{aligned} \quad (40)$$

where the transformation of the spatial function parameters upon the linear transformation,  $\mathbf{P}_p^r$ , of the coordinates was inserted, Eqs. (18)–(27), and for brevity the following notation was introduced:

$$\tilde{\kappa}_p(\boldsymbol{\vartheta}) = (\mathbf{P}_p^s)^T \kappa(\boldsymbol{\vartheta}) \quad (41)$$

and

$$\mathbf{u}_p^{(0)} = (\mathbf{P}_p^r)^T \mathbf{u}^{(0)} \quad \text{and} \quad \mathcal{A}_p^{(0)} = (\mathbf{P}_p^r)^T \mathcal{A}^{(0)} \mathbf{P}_p^r. \quad (42)$$

## D. Overlap and Hamiltonian matrix elements

The matrix element of a spin-independent and permutationally invariant operator,  $\hat{O}$ , for basis functions  $I$  and  $J$  is evaluated as

$$\begin{aligned} O_{IJ}^{[\lambda],[\zeta]} &= \langle \Phi_I^{[\lambda],[\zeta]} | \hat{O} | \Phi_J^{[\lambda],[\zeta]} \rangle_{r,\sigma} \\ &= \langle \hat{\mathcal{A}} \{ \phi_I^{[\lambda]} \chi_I^{[\zeta]} \} | \hat{O} | \hat{\mathcal{A}} \{ \phi_J^{[\lambda]} \chi_J^{[\zeta]} \} \rangle_{r,\sigma}. \end{aligned} \quad (43)$$

By exploiting the quasi-idempotency  $\hat{\mathcal{A}}\hat{\mathcal{A}} = (N_{\text{perm}})^{1/2}\hat{\mathcal{A}}$ , the  $(I\text{th}, J\text{th})$  matrix element is

$$\begin{aligned} O_{IJ}^{[\lambda, \varsigma]} &= \sum_{p=1}^{N_{\text{perm}}} \varepsilon_p \langle \phi_I^{[\lambda]} \chi_I^{[\varsigma]} | \hat{O} | \hat{P}_p \{ \phi_J^{[\lambda]} \chi_J^{[\varsigma]} \} \rangle_{r, \sigma} \\ &= \sum_{p=1}^{N_{\text{perm}}} \varepsilon_p \langle \phi_I^{[\lambda]} | \hat{O} | \hat{P}_p \phi_J^{[\lambda]} \rangle_r \langle \chi_I^{[\varsigma]} | \hat{P}_p \chi_J^{[\varsigma]} \rangle_\sigma \\ &= \sum_{p=1}^{N_{\text{perm}}} c_{IJ_p}^{[\varsigma]} O_{IJ_p}^{[\lambda]} \end{aligned} \quad (44)$$

with

$$c_{IJ_p}^{[\varsigma]} = \varepsilon_p \langle \chi_I^{[\varsigma]} | \hat{P}_p \chi_J^{[\varsigma]} \rangle_\sigma, \quad (45)$$

$$O_{IJ_p}^{[\lambda]} = \langle \phi_I^{[\lambda]} | \hat{O} | \hat{P}_p \phi_J^{[\lambda]} \rangle_r. \quad (46)$$

In this work,  $\hat{O}$  will be the unit operator,  $\hat{T}$ , the kinetic energy operator,  $\hat{T}$ , and the potential energy operator,  $\hat{V}$ . Accordingly, the overlap matrix element is

$$S_{IJ}^{[\lambda, \varsigma]} = \sum_{p=1}^{N_{\text{perm}}} c_{IJ_p}^{[\varsigma]} S_{IJ_p}^{[\lambda]} \quad \text{with} \quad S_{IJ_p}^{[\lambda]} = \langle \phi_I^{[\lambda]} | \hat{P}_p \phi_J^{[\lambda]} \rangle_r. \quad (47)$$

The matrix elements for the kinetic and the potential energy operators are

$$T_{IJ}^{[\lambda, \varsigma]} = \sum_{p=1}^{N_{\text{perm}}} c_{IJ_p}^{[\varsigma]} T_{IJ_p}^{[\lambda]} \quad \text{with} \quad T_{IJ_p}^{[\lambda]} = \langle \phi_I^{[\lambda]} | \hat{T} | \hat{P}_p \phi_J^{[\lambda]} \rangle_r \quad (48)$$

and

$$V_{IJ}^{[\lambda, \varsigma]} = \sum_{p=1}^{N_{\text{perm}}} c_{IJ_p}^{[\varsigma]} V_{IJ_p}^{[\lambda]} \quad \text{with} \quad V_{IJ_p}^{[\lambda]} = \langle \phi_I^{[\lambda]} | \hat{V} | \hat{P}_p \phi_J^{[\lambda]} \rangle_r \quad (49)$$

so that

$$H_{IJ}^{[\lambda, \varsigma]} = T_{IJ}^{[\lambda, \varsigma]} + V_{IJ}^{[\lambda, \varsigma]}. \quad (50)$$

Then, we are left with the evaluation of  $S_{IJ_p}^{[\lambda]}$ ,  $T_{IJ_p}^{[\lambda]}$ , and  $V_{IJ_p}^{[\lambda]}$ , i.e., the matrix elements for two spatial functions, Eqs. (12) and (14). The procedure (see, for example, Ref. 35) is somewhat tedious, so we list here only the main steps of the evaluation and collect the explicit formulae in the supplementary material.

A matrix element of operator  $\hat{O}$  is best written using the form of the basis function given with the generating integral equation (14), and it is, with  $\lambda = (L, M_L, p)$ ,

$$\begin{aligned} &\langle \phi^{[\lambda]}(\mathbf{r}; \mathcal{A}, \mathbf{u}, K) | \hat{O} | \phi^{[\lambda]}(\mathbf{r}; \mathcal{A}', \mathbf{u}', K') \rangle_r \\ &= \frac{1}{\mathcal{B}_{KLp} \mathcal{B}_{K'Lp}} \int d\hat{\mathbf{e}} \int d\hat{\mathbf{e}}' \eta_{LM_Lp}^*(\hat{\mathbf{e}}) \eta_{LM_Lp}(\hat{\mathbf{e}}') \\ &\quad \times \{ \hat{\mathcal{D}}_a^{(2K+L)} \hat{\mathcal{D}}_{a'}^{(2K'+L)} \\ &\quad \langle g(\mathbf{r}; \mathcal{A}, s(\mathbf{a}, \mathbf{u}, \mathbf{e})) | \hat{O} | g(\mathbf{r}; \mathcal{A}', s'(\mathbf{a}', \mathbf{u}', \mathbf{e}')) \rangle_r \}_{a_i=a'_i=0, |\mathbf{e}_i|=|\mathbf{e}'_i|=1}. \end{aligned} \quad (51)$$

The definition of the symbols is given in Table I and the integration is carried out over the points of the unit sphere de-

scribed by the spherical angles collected in  $\hat{\mathbf{e}}$  and  $\hat{\mathbf{e}}'$  of the unit vectors  $\mathbf{e}$  and  $\mathbf{e}'$ , respectively.  $\langle \dots \rangle_r$  indicates that the integration has to be carried out for the spatial coordinates  $\mathbf{r}$ .

The evaluation of the integral in Eq. (51) includes the following steps.

- (1) Evaluation of the integral with the generating functions (floating geminals)

$$I_{O,1}(s, s') = \langle g(\mathbf{r}; \mathcal{A}, s) | \hat{O} | g(\mathbf{r}; \mathcal{A}', s') \rangle_r. \quad (52)$$

- (2) Differentiation prescribed by the operators  $\hat{\mathcal{D}}_a^{(2K+L)}$  and  $\hat{\mathcal{D}}_{a'}^{(2K'+L)}$  (see Table I for the definition). Then, the result is expressed in terms of polynomials of scalar products of the unit vectors,  $\mathbf{e}^T \mathbf{e}'$ ,

$$\begin{aligned} I_{O,2}^{[L]}(\mathbf{e}, \mathbf{e}') &= \left\{ \hat{\mathcal{D}}_a^{(2K+L)} \hat{\mathcal{D}}_{a'}^{(2K'+L)} \right. \\ &\quad \left. I_{O,1}(s(\mathbf{a}, \mathbf{u}, \mathbf{e}), s'(\mathbf{a}', \mathbf{u}', \mathbf{e}')) \right\}_{a_i=a'_i=0, |\mathbf{e}_i|=|\mathbf{e}'_i|=1}. \end{aligned} \quad (53)$$

- (3) Evaluation of the angular integrals

$$\begin{aligned} I_{O,3}^{[\lambda=(L, M_L, p)]} &= \frac{1}{\mathcal{B}_{KLp} \mathcal{B}_{K'Lp}} \int d\hat{\mathbf{e}} \\ &\quad \times \int d\hat{\mathbf{e}}' \eta_{LM_Lp}^*(\hat{\mathbf{e}}) \eta_{LM_Lp}(\hat{\mathbf{e}}') I_{O,2}^{[L]}(\mathbf{e}, \mathbf{e}'), \end{aligned} \quad (54)$$

which reads for the natural-parity case,  $p = (-1)^L$ , as

$$\begin{aligned} I_{O,3}^{[\lambda=(L, M_L, (-1)^L)]} &= \frac{1}{\mathcal{B}_{KLp} \mathcal{B}_{K'Lp}} \int d\hat{\mathbf{e}} \\ &\quad \times \int d\hat{\mathbf{e}}' Y_{LM_L}^*(\hat{\mathbf{e}}) Y_{LM_L}(\hat{\mathbf{e}}') I_{O,2}^{[L]}(\mathbf{e}, \mathbf{e}'). \end{aligned} \quad (55)$$

The evaluation of the angular integrals is facilitated by the identity, see p. 87 of Ref. 35, related to the addition theorem of spherical harmonics

$$(\mathbf{e}^T \mathbf{e}')^k = \sum_{l=0}^k B_{\frac{k-l}{2}, l} \sum_{m=-l}^l Y_{lm}^*(\hat{\mathbf{e}}) Y_{lm}(\hat{\mathbf{e}}'), \quad (56)$$

$[(k-l)/2 \in \mathbb{N}_0]$

which is for  $k = 1$

$$\mathbf{e}^T \mathbf{e}' = \frac{4\pi}{3} \sum_{m=-1}^1 Y_{1m}^*(\hat{\mathbf{e}}) Y_{1m}(\hat{\mathbf{e}}'). \quad (57)$$

Further details of the derivation of the overlap, kinetic, and potential energy integrals are given in the supplementary material.

For large  $(2K + L) > 4$  exponents of the  $|\mathbf{v}|^{2K+L}$  polynomial prefactor, Eq. (12), a direct implementation of the integral formulae given in Refs. 35 and 53 resulted in numerical instabilities for a computer program with a finite number representation (double precision in FORTRAN). To restore the numerical stability, we introduced quasi-normalization for the basis functions, which allowed us to cancel some problematic terms. We call the normalization with respect to the spatial function,

$$\Phi^{[\lambda, \varsigma]} = (\langle \phi^{[\lambda]} | \phi^{[\lambda]} \rangle_r)^{-1/2} \hat{\mathcal{A}} \{ \phi^{[\lambda]} \chi^{[\varsigma]} \}, \quad (58)$$



quasi-normalization. The quasi-normalized and rearranged integral formulae are collected in the supplementary material. Where it was necessary and useful, we used a logarithmic evaluation of products and fractions, e.g.,

$$(a \cdot b)/(c \cdot d) = \text{sign}(ab/cd) \cdot 10^{(\lg a + \lg b - \lg c - \lg d)}, \quad (59)$$

which allowed us to obtain small numbers as ratios and products of large ones. Furthermore, it was possible to factor out the term, see the supplementary material,

$$F_{KL} = \sum_{m=0}^K \frac{2^{2m}(L+m+1)!}{(K-m)!(K-m)!m!(2L+2m+2)!}, \quad (60)$$

whose value for a finite number of  $K$  and  $L$  integer values was pre-calculated with MATHEMATICA.<sup>80</sup> These numbers were stored in a file and are read in by the FORTRAN program.

## E. Multi-stage variational optimization

The wave function for some set of quantum numbers  $\lambda = (L, M_L, p)$  and  $\varsigma = (S, M_S)$  is written as a linear combination of  $N_b$  basis functions

$$\begin{aligned} \Psi^{[\lambda, \varsigma]}(\mathbf{r}, \boldsymbol{\sigma}) &= \sum_{I=1}^{N_b} c_I \Phi_I^{[\lambda, \varsigma]}(\mathbf{r}, \boldsymbol{\sigma}) \\ &= (N_{\text{perm}})^{-1/2} \sum_{I=1}^{N_b} c_I \\ &\quad \times \sum_{p=1}^{N_{\text{perm}}} \hat{P}_p \{ \phi^{[\lambda]}(\mathbf{r}; \boldsymbol{\alpha}_I, \mathbf{u}_I, K_I) \chi^{[\varsigma]}(\boldsymbol{\sigma}; \boldsymbol{\vartheta}_I) \}. \end{aligned} \quad (61)$$

The concept of this parameterization is visualized in Figure 3. Since the overlap and the Hamiltonian matrix elements are evaluated analytically (Sec. II D and the supplementary material), we can rely on the variational principle during the course of the selection of the numerical values for the “free parameters” of this ansatz. Thus, the lower the eigenenergy, the better the parameterization is. During the course of the calculations we tightened the optimization criterion of the free parameters and increased the number of the basis functions to obtain a lower energy eigenvalue.

In this work, we solved the generalized linear variational problem corresponding to  $N_b$  basis functions with some fixed

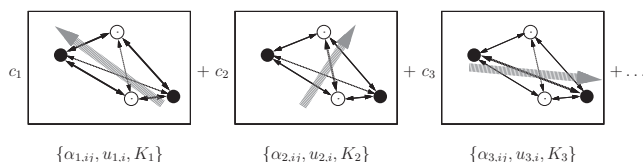


FIG. 3. Visual representation of the parameterization of the wave function for  $H_2$ . The width of the lines of the double-headed arrows, which connect the particles  $i$  and  $j$  is proportional to the value of  $\alpha_{I,ij}$  ( $i = 1, \dots, 4$ ;  $j = i + 1, \dots, 4$ ), and the orientation of the grey arrows represent the orientation of the global vectors parameterized by  $u_{I,i}$  ( $i = 1, 2, 3$ ) ( $I = 1, 2, \dots, N_b$ ).

$\mathcal{P}_I = (\boldsymbol{\alpha}_I, \mathbf{u}_I, K_I; \boldsymbol{\vartheta}_I)$  parameters

$$\mathbf{H}^{[\lambda, \varsigma]} \mathbf{c}_i^{[\lambda, \varsigma]} = E_i^{[\lambda, \varsigma]} \mathbf{S}^{[\lambda, \varsigma]} \mathbf{c}_i^{[\lambda, \varsigma]} \quad i = 1, 2, \dots, N_b \quad (62)$$

using the LAPACK “divide and conquer” diagonalizer available in Intel’s Math Kernel Library (MKL).<sup>81</sup> If the parameter set,  $\mathcal{P}_I$ , was selected appropriately (see the discussion below), we did not observe any near-linear dependency problems in finite-precision, 8-byte (double precision in FORTRAN), arithmetics. Near-linear dependency problems were always indicators of an inadequate parameter generation.

The parameters were generated for one basis function after the other in a random procedure.<sup>30,35,64–66</sup> The random generation with a variational selection criterion is a straightforward approach, and this explains our choice here. We have found the description in Ref. 35 the most useful in our work, including the fast eigenvalue estimation procedure of an updated parameter set, described on pp. 27–29 of Ref. 35.

In addition, we have investigated the effect of the coordinate representation and the sampling strategy on the convergence rate of the energy with respect to the computational effort. We have found that both have a crucial impact on the efficiency, and we summarize our observations and our strategy developed as follows.

### 1. Non-linear variational problem

Optimization of the parameters of the basis functions is a delicate problem. For example, for an  $(n_p + 1)$ -particle system there are  $(n_p + 1)n_p/2 + n_p + 1 = (n_p + 1)(n_p + 2)/2$  free parameters,  $\{\boldsymbol{\alpha}_I, \mathbf{u}_I, K_I\}$ , corresponding to each spatial function, Eqs. (12) and (13). If, for example,  $n_p + 1 = 4$ , there are 10 free parameters for each basis function, and thus for 500 basis functions, the ansatz contains 5000 parameters to be optimized. One may suspect that there is a myriad of local minima for such a large number of free parameters. Nevertheless, the variational principle and the physical-chemical intuition served as two major guiding tools for us in the construction of a useful strategy for calculating as low of an energy eigenvalue (and the corresponding wave function) as possible. The actual values of the free parameters at the minimum point are not of primary interest, and there might be several equivalent or at least “almost equivalent” parameterizations due to the non-orthogonality of the basis functions and the multiple equivalent coordinate representations.

During the course of the buildup of the basis set, the free parameters were optimized one after the other. To select a new parameter a large number of trial values were generated randomly, which were then tested using the fast eigenvalue-update procedure of Ref. 35. Then, that trial value was utilized for the extension of the basis set, which provided the lowest energy eigenvalue (or the lowest few energy eigenvalues if vibrational excited states were also of interest). For small to medium-sized basis sets (with typically 50–200 basis functions), we run regular refinement cycles for the already selected parameters, which allowed us to replace an earlier selected parameter with a newly generated and better one, i.e., which corresponded to a lower energy eigenvalue.

In order to select parameters for new spatial and spin functions, we had to generate and test trial values for the

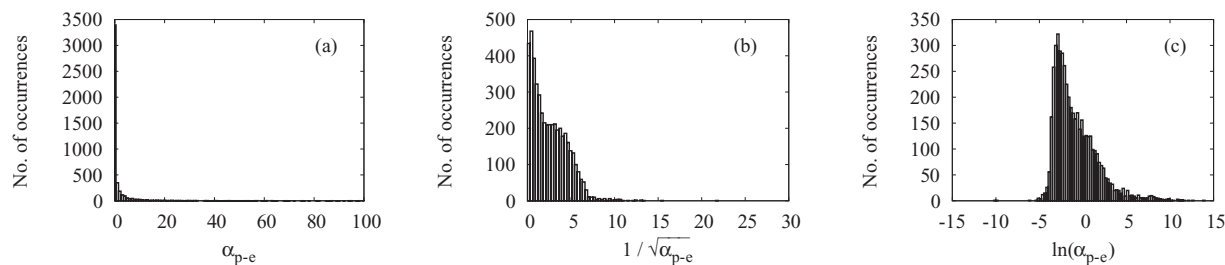


FIG. 4. Optimized basis function parameters for  $H_2$  ( $L = 0$ ,  $p = +1$ ,  $S_p = 0$ ,  $K_{\max} = 10$ ). The  $\alpha_{p-e}$  exponents corresponding to laboratory-fixed Cartesian coordinates were optimized using  $\xi = (\alpha_{p-e})^{-1/2}$  and a random number generator with a uniform continuous distribution of  $\xi \in u(a_{\min}^{(p-e)}, a_{\max}^{(p-e)})$ . The  $K$  values were generated (not optimized) in a uniform discrete distribution with  $[0, K_{\max}]$ .

$K \in \mathbb{N}_0$  polynomial exponent, the  $\alpha_{ij} \in \mathbb{R}^+$  Gaussian exponents (or the entries of the symmetric  $\mathcal{A}^{(0)}$  or  $\mathcal{A}^{(x)}$  matrices), the  $u_i \in \mathbb{R}$  (or  $\mathbf{u}_i$ ) global vector parameters, and, in the case of the three-fermionic  $^7\text{Li}$ , the  $\vartheta_1 \in [-\pi/2, \pi/2]$  spin-function parameter. As to the efficiency of this trial-and-error optimization, we had to address a few technical questions:

1. Shall we sample the parameters corresponding to the laboratory-fixed Cartesian coordinate representation, i.e.,  $\alpha_{ij}$  and  $\mathcal{A}_{ij}^{(0)}$ , or is it better to generate first the trial parameters corresponding to some  $\mathbf{x}$  translationally invariant set of coordinates,  $\mathcal{A}_{ij}^{(x)}$ ?

In general, which is the most convenient coordinate set for the optimization?

2. Shall we generate random values for the original parameter, say  $\alpha_{ij}$ , or shall we use instead a transformed one, e.g.,  $\sqrt{\alpha_{ij}}$  or  $\ln \alpha_{ij}$ ?

In general, what kind of probability distribution shall we use in the random number generator to generate random trials efficiently for the selected parameterization and coordinate representation?

In the calculations, we used the quasi-random number generators of the Vector Statistical Library available in Intel's MKL.<sup>81</sup> The intrinsic randomness or quasi-randomness of the trials did not play a role here.

The first question is related to the quasi-separability of the many-particle correlation problem to some, coupled, few-particle correlations represented by some coordinate set, Figure 2, and the corresponding geminal basis. The second question addresses the characteristic values and the distribution of the parameters in some representation. In an ideal case, all parameters,  $A_{12}, A_{13}, \dots, u_1, u_2, \dots$  could be optimized independently and the optimal values would be distributed according to some ordinary probability distribution, which is characterized by a few, well-defined parameters. Then, the generation of a trial value according to this probability distribution would be a reasonable first guess, not far from a real minimum point. In practice, a brute-force treatment of a few-particle system can be far from this ideal case, but it can be approached by a good choice of the coordinate set.

Assuming that a coordinate set has been selected, we give an example to our second question in Figure 4, which presents histograms for the optimized values of the proton-electron correlation exponents corresponding to the ground state of the  $H_2$  molecule. As it is apparent from the figure, it is the most practical to sample the distribution of  $\ln \alpha_{p-e}$ , instead of  $\alpha_{p-e}$ .

After exploratory test calculations, we estimated the envelope of the histograms with a normal probability density function parameterized with the sample mean and the unbiased sample variance and used this random distribution in our large-scale calculations to generate “reasonable” trial values for the optimization. In principle, it would be possible to automatize this procedure in the spirit of a sampling-importance-resampling strategy.<sup>82</sup> We note here that the sampling of a uniform continuous distribution for  $\alpha_{ij}$  resulted in a very slow convergence rate and near-linear dependence problems in finite precision arithmetics. In any case, we conclude that the parameterization and the random distribution, which we sample, have a (sometimes dramatic) influence on the convergence rate. At the same time, the convergence is guaranteed, in theory, by the variational principle.

## 2. Basis function generation strategy

We can summarize our basis function generation strategy as follows.

1.  $K$  was generated (not optimized) according to some discrete uniform or discretized normal distribution with the sample mean and the unbiased sample variance determined in test calculations, similar to Refs. 36, 83, and 84.
2. In the case of lithium,  $\vartheta_1$  was generated (not optimized) according to a uniform continuous distribution over the interval  $[-\pi/2, \pi/2]$ .
3. Trial values of  $\ln \alpha_{ij}$  corresponding to LF Cartesian coordinates were generated according to a normal distribution with some sample mean and some unbiased sample variance determined in test calculations. That trial value

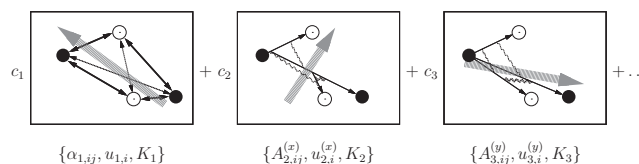


FIG. 5. Visual representation of an ansatz for the  $H_2$  molecule expressed in terms of several coordinates (channels). The Gaussian geminal exponents represented by double-headed arrows and wavy lines correspond to (1) laboratory-fixed Cartesian coordinates; (2) Jacobi coordinates; (3) heavy-particle centered coordinates, respectively, where the different widths of the lines represent the different numerical values of the various exponents. The grey arrows indicate the orientation of the global vectors parameterized by  $u_{l,i}$  ( $i = 1, 2, 3$ ) ( $l = 1, 2, 3, \dots, N_b$ ).

was selected for the construction of the basis function, which provided the lowest energy eigenvalue.

4. Trial values of  $u_i^{(x)}$  ( $i = 1, 2, \dots, n_p$ ) were generated according to a normal distribution with some sample mean and some unbiased sample variance determined in test calculations. That trial value was selected for the construction of the basis function, which provided the lowest energy eigenvalue. Instead of using LF Cartesian coordinates, a set of translationally invariant coordinates,  $\mathbf{x}$ , was selected, which described reasonably well the angular distribution of the particles. In the case of  $\text{H}_2$ , the atoms-in-molecule coordinates (Sec. III) were found to provide a useful representation, similar to  $\text{Ps}_2$ .<sup>85</sup>

During the extension of the basis set, we regularly run refinement cycles for the already selected Gaussian exponents,  $\alpha_{ij}$ , and the global vector coefficients,  $u_i^{(x)}$ , using the same random number distributions as before, while the values of the  $K$  and  $\vartheta_1$  parameters were kept fixed.

Finally, the  $\alpha_{ij}$  and the  $u_i^{(x)}$  values were further optimized in repeated fine-tuning cycles based on random walks. The fine-tuning was carried out for each  $\alpha_{ij}$  and  $u_i$  parameter one after the other, and was started from the original value of the parameter. A new value was accepted or rejected based on the variational principle. During the random walk, the parameter values were not restricted within any interval, but they were controlled by the definition of a “fine-tuning” radius, which allowed the program to change the parameter value with a certain percentage only, and each random walk sequence was limited by a maximum number of steps.

The optimization of the Gaussian exponents and the global vector parameters were carried out in terms of *different* coordinates. Due to the simple transformation property of the basis functions (and thus the integrals) in terms of a linear transformation of the coordinates, one can use several coordinate representations during the *same* calculation (“re-parameterization”). As a result of this observation, we propose a multiple-coordinate or multiple-channel optimization strategy.

### 3. Multiple-channel optimization

Our optimization strategy needs to answer the questions of how to guess a “good enough” coordinate representation for the optimization procedure and what the best strategy to follow is if there are more than one coordinate representa-

tions which describe important but qualitatively different few-particle correlations?

Since the re-parameterization of the basis functions in terms of various sets of Cartesian coordinates is straightforward, one can optimize (generate and test, refine, and fine-tune) the basis function parameters using several coordinate representations, Figure 5.

A simple application of this multiple-channel optimization strategy is used in our present optimization procedure (steps 1–4), but it can, of course, be generalized by relying on several coordinate representations.

## III. NUMERICAL RESULTS

We have implemented the theory outlined to study the ground and some excited states of  $\text{H}_2^+$ ,  $\text{Ps}_2$ ,  $\text{H}_2$ , and  $^7\text{Li}$ . As characteristic properties of these systems, the mass, the electric charge, and the spin of the particles as well as the spatial angular momentum and the spin quantum numbers were specified, while we considered states with natural parity only. The virial coefficient,  $\eta = |1 + \langle \Phi | \hat{V} | \Phi \rangle / 2 \langle \Phi | \hat{T} | \Phi \rangle|$ , was evaluated to assess the quality of the calculated wave functions.

During the course of the non-linear optimization the  $\ln \alpha_{ij}$  coefficients were generated and optimized corresponding to the LF Cartesian coordinates where the  $\alpha_{ij}$  parameter is the exponent corresponding to the square of the Cartesian displacement vector between the  $i$ th and  $j$ th particles, Eq. (12). The global vector coefficients were generated and optimized using the translationally invariant coordinates shown in Figure 6.

After the selection and refinement of the  $\alpha_{ij}$  and  $u_i$  parameters, we ran repeated fine-tuning cycles by carrying out random walk sequences, which started from the original value and with a random but less than 10% change of the actual value. A new value was accepted if it lowered the total energy.

Before we discuss the results obtained, we should stress that due to omission of the BO paradigm, no potential energy surface with respect to a subset of coordinates is obtained. Instead, we obtain the total energies and thus all but one are excited states.

### A. $\text{H}_2^+$

Figure 7 summarizes our results for  $\text{H}_2^+$  and the corresponding BO potential energy curves are also sketched for

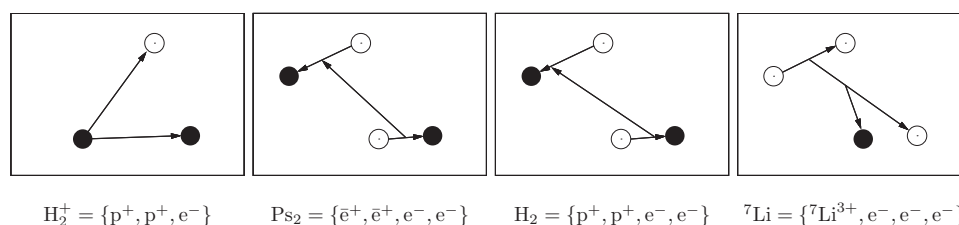


FIG. 6. The translationally invariant Cartesian coordinates used for the optimization of the global vector coefficients. The empty and the full circles represent the electrons and the positively charged particles, respectively.  $\text{H}_2^+$ : proton-centered coordinates (similar to heavy-particle centered coordinates<sup>35</sup>);  $\text{Ps}_2$  and  $\text{H}_2$ : “atoms-in-molecule” coordinates<sup>85</sup> (AIM- $\text{Ps}_2$  and AIM- $\text{H}_2$ , respectively), where the “inter-atomic” distance vector connects the center-of-mass points of the two “subatoms”;  $^7\text{Li}$ : Jacobi coordinates.<sup>35</sup>

TABLE II. Calculated energy levels of  $H_2^+ = \{p^+, p^+, e^-\}$ .

$L^a$	$p^a$	$S_p^a$	$E/E_h^b$	$\eta^c$	$\delta E/\mu E_h^d$	Ref.	Assignment <sup>e</sup>
0	1	0	-0.597139059	$1.6 \times 10^{-8}$	-0.004	89, 90	para $\tilde{X}^2\Sigma_g^+ v=0$
0	1	0	-0.587155670	$3.2 \times 10^{-9}$	-0.009	89, 90	para $\tilde{X}^2\Sigma_g^+ v=1$
[...]							
1	-1	1	-0.596873733	$7.9 \times 10^{-9}$	-0.005	89, 90	ortho $\tilde{X}^2\Sigma_g^+ v=0$
1	-1	1	-0.586904311	$9.4 \times 10^{-8}$	-0.010	89, 90	ortho $\tilde{X}^2\Sigma_g^+ v=1$
[...]							
2	1	0	-0.596345202	$1.8 \times 10^{-8}$	-0.004	89, 90	para $\tilde{X}^2\Sigma_g^+ v=0$
2	1	0	-0.586403620	$1.4 \times 10^{-7}$	-0.011	89, 90	para $\tilde{X}^2\Sigma_g^+ v=1$
[...]							
3	-1	1	-0.595557635	$4.1 \times 10^{-10}$	-0.004	90	ortho $\tilde{X}^2\Sigma_g^+ v=0$
3	-1	1	-0.585657606	$1.6 \times 10^{-8}$	-0.006	90	ortho $\tilde{X}^2\Sigma_g^+ v=1$
[...]							
4	1	0	-0.594517166	$2.0 \times 10^{-9}$	-0.003	90	para $\tilde{X}^2\Sigma_g^+ v=0$
4	1	0	-0.584672130	$4.0 \times 10^{-8}$	-0.004	90	para $\tilde{X}^2\Sigma_g^+ v=1$
[...]							
5	-1	1	-0.593231725	$6.4 \times 10^{-9}$	-0.004	88	ortho $\tilde{X}^2\Sigma_g^+ v=0$
5	-1	1	-0.583454791	$1.6 \times 10^{-8}$	-0.005	88	ortho $\tilde{X}^2\Sigma_g^+ v=1$
[...]							
0	1	1	-0.499743489	$1.1 \times 10^{-8}$	-0.014	88	ortho $\tilde{A}^2\Sigma_u^+ v=0$
1	-1	0	-0.499739262	$1.5 \times 10^{-8}$	-0.006	88	para $\tilde{A}^2\Sigma_u^+ v=0$
2	1	1	-0.499731516	$1.9 \times 10^{-8}$	-0.007	88	ortho $\tilde{A}^2\Sigma_u^+ v=0$

<sup>a</sup> $L$ : quantum number of the total angular momentum without the spins;  $p$ : parity;  $S_p$ : total spin quantum number of the protons.

<sup>b</sup> $m_p/m_e = 1836.15267247$ .<sup>86</sup> The dissociation limit is  $E(H(n=1)) = -0.499727840 E_h$ . The wave functions were optimized as a linear combination of  $N_b = 400$  basis functions and for the exponents  $2K$  of the polynomial prefactors the  $K$  values were generated in a normal distribution with mean and variance 5 and 1, respectively, and then the generated value was rounded to the nearest integer.

<sup>c</sup> $\eta = |1 + \langle \Psi | \hat{V} | \Psi \rangle / (2 \langle \Psi | \hat{T} | \Psi \rangle)|$ .

<sup>d</sup> $\delta E = E(\text{Ref.}) - E$ .

<sup>e</sup>The assignment of the ortho ( $S_p = 1$ ) and para ( $S_p = 0$ ) descriptions corresponds to the value of the  $S_p$  quantum number. The electronic state label of the BO theory is assigned based on comparison with the literature.<sup>87,88</sup> There are two energy levels shown corresponding to every set of  $(L, p, S_p)$  quantum numbers in the electronic ground state, which can be assigned to the ground and the first excited vibrational energy levels of the BO theory.

comparison. The calculated numerical values are given in Table II. We used a proton-electron mass ratio of  $m_p/m_e = 1836.15267247$ .<sup>86</sup> The corresponding non-relativistic ground-state energy of the free hydrogen atom, which is the dissociation limit, is  $E(H) = -0.499727840 E_h$ .

The quantum numbers of the non-relativistic theory are  $L$ ,  $p$ , and  $S_p$ . To obtain the various energy levels shown in

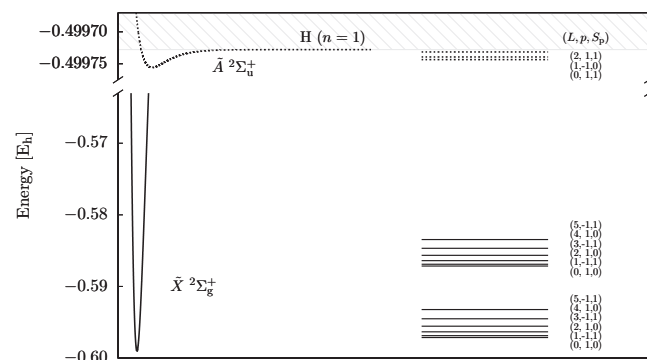


FIG. 7. Calculated all-particle (pre-Born-Oppenheimer) energy levels of  $H_2^+$  (on the right). For comparison, the Born-Oppenheimer potential energy curves are also illustrated (on the left). The dissociation energy corresponds to the ground state energy of the hydrogen atom. The numerical values of the calculated energy levels are given in Table II.  $L$ : Total angular momentum quantum number without the spins,  $p = (-1)^L$ : parity, and  $S_p$ : the total spin quantum number of the protons.

Figure 7, we chose various values for  $L$  and  $S_p$ , and always assumed natural parity,  $p = (-1)^L$ . Due to the Pauli principle for the protons, if the internal part of the wave function is symmetric with respect to the interchange of the two protons for even (odd)  $L$ , the total spin of the protons,  $S_p$  must be 0 (1), i.e., para- $H_2^+$  (ortho- $H_2^+$ ). This case can be assigned to the rotation-vibration energy levels of the electronic ground state,  $\tilde{X}^2\Sigma_g^+$ , of standard BO-based theory. On the other hand, if the internal part of the wave function is antisymmetric with respect to the interchange of the two protons for even (odd)  $L$ ,  $S_p$  must be 1 (0), i.e., ortho- $H_2^+$  (para- $H_2^+$ ). This case corresponds to the electronically excited state,  $\tilde{A}^2\Sigma_u^+$  of BO theory.

The numerical results are compared to literature data, Table II, and the agreement with for example, Refs. 87–90 is good. As to the  $\tilde{A}^2\Sigma_u^+$  states, we obtained only three rotation-only (vibrational ground state) energy levels below the dissociation limit, in agreement with earlier calculations.<sup>87,88</sup>

## B. $Ps_2$

Our second example is the positronium molecule ( $Ps_2$ ), with four particles of equal mass, two of them positively charged and two of them negatively charged. Variational calculations without the adiabatic separation of the positive and



TABLE III. Calculated energy levels of the positronium molecule,  $\text{Ps}_2 = \{\bar{e}^+, \bar{e}^+, e^-, e^-\}$ .

$L^a$	$p^a$	$S_+^a$	$S_-^a$	$E/E_h^b$	$\eta^c$	$\delta E/\mu E_h^d$	Ref.	Assignment <sup>e</sup>
0	1	0	0	-0.5160037887	$3.9 \times 10^{-9}$	-0.0017	97	$0^+ A_1$
0	1	1	0	-0.3302874964	$3.3 \times 10^{-8}$	+10.686	85	$0^+ E$
1	-1	0	0	-0.3344082953	$1.8 \times 10^{-8}$	-0.022	99	$1^- B_2$

<sup>a</sup> $L$ : quantum number of the total angular momentum without the spins;  $p$ : parity;  $S_+$  and  $S_-$ : total spin quantum number of the positrons,  $\bar{e}^+$ , and that of the electrons,  $e^-$ , respectively.

<sup>b</sup> $m_+/m_- = 1$ . The energy of the lowest-lying dissociation threshold is  $E(\text{Ps}(n=1) + \text{Ps}(n=1)) = -1/2 E_h = -0.5 E_h$ , while the second two states belong to a different symmetry block, and the corresponding dissociation threshold is  $E(\text{Ps}(n=1) + \text{Ps}(n=2)) = -5/16 E_h = -0.3125 E_h$ .<sup>85</sup> The wave functions were optimized as a linear combination of  $N_b = 1200$  basis functions and the exponents of the polynomial prefactors were  $2K = 0$  or  $2$ , selected randomly.

<sup>c</sup> $\eta = |1 + \langle \Psi | \hat{V} | \Psi \rangle / (2 \langle \Psi | \hat{T} | \Psi \rangle)|$ .

<sup>d</sup> $\delta E = E(\text{Ref.}) - E$ .

<sup>e</sup> $L^p$  and the symmetry labels are taken from Refs. 33 and 85.

negative particles were presented already in 1947 (Ref. 91) and later more accurate calculations for the ground,<sup>33,34,92,93</sup> excited,<sup>85,94,95</sup> and possible metastable states<sup>33,96</sup> followed.

Bound states must lie below the lowest-energy dissociation limit, and the states above are in the continuum. There are however different symmetry blocks or spin states which are not coupled to the continuum of the lowest-lying dissociation products, and thus they can be calculated within the present approach.

We considered here only three states, which are known to be bound.<sup>85</sup> Our  $L = 0$  and  $L = 1$  calculations, Table III, with zero spins agree well with the best available literature data.<sup>97,98</sup> For all three states, we obtain substantially lower energies than those of Ref. 85 and the results could be further improved by extended optimization times. In this work, we have not considered the fourth known bound state, which would become easily accessible to the present approach by considering the charge conjugation symmetry, a special property of this system.

## C. H<sub>2</sub>

Figure 8 summarizes our results for the H<sub>2</sub> molecule and the numerical results are collected in Table IV. With various

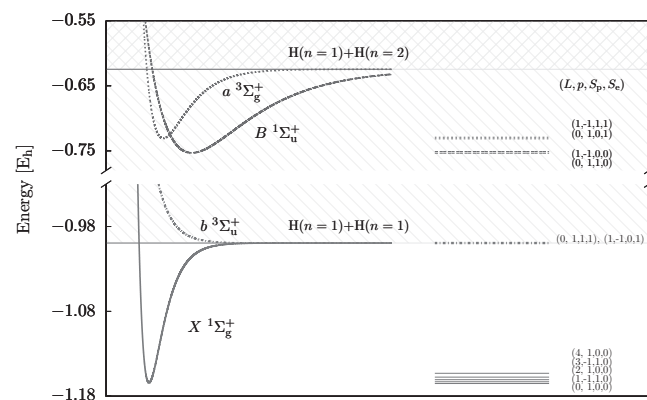


FIG. 8. Calculated all-particle (pre-Born-Oppenheimer) energy levels of H<sub>2</sub> (on the right). For comparison the Born-Oppenheimer potential energy curves are also illustrated (on the left). The lower- and the higher-energy dissociation thresholds shown in the figure correspond to two hydrogen atoms in the ground state, and to one hydrogen atom in the ground state and the other in the first excited state, respectively. The numerical values of the calculated energy levels are given in Table IV.  $L$ : quantum number of the total angular momentum without the spins,  $p = (-1)^L$ : parity,  $S_p$ : the total spin quantum number of the protons, and  $S_e$ : the total spin quantum number of the electrons.

selections for the quantum number of the total angular momentum without the spins,  $L$ , the total proton spin,  $S_p$ , and the total electron spin,  $S_e$ , the lowest energy levels of four “types” (symmetries) of states became easily accessible, while we always considered natural parity,  $p = (-1)^L$ . These four “symmetry cases” (or “spin cases”) are

- (1)  $L = 0, 1, \dots, p = (-1)^L, S_e = 0$  (singlet),  $S_p = (1 - p)/2$  (para for even  $L$ , ortho for odd  $L$ );
- (2)  $L = 0, 1, \dots, p = (-1)^L, S_e = 1$  (triplet),  $S_p = (1 - p)/2$  (para for even  $L$ , ortho for odd  $L$ );
- (3)  $L = 0, 1, \dots, p = (-1)^L, S_e = 0$  (singlet),  $S_p = (1 + p)/2$  (ortho for even  $L$ , para for odd  $L$ );
- (4)  $L = 0, 1, \dots, p = (-1)^L, S_e = 1$  (triplet),  $S_p = (1 + p)/2$  (ortho for even  $L$ , para for odd  $L$ ).

The four cases are assigned, based on direct comparison of the calculated energy levels with the literature, to the  $X^1\Sigma_g^+$ ,<sup>47</sup>  $b^3\Sigma_u^+$  (repulsive),<sup>100</sup>  $B^1\Sigma_u^+$ ,<sup>101-106</sup> and  $a^3\Sigma_g^+$  (Refs. 101, 107, and 108) electronic states of the BO theory, respectively. These electronic states are the four lowest ones of the hydrogen molecule.<sup>109</sup> The corresponding potential energy functions are visualized in Figure 8 (for their calculation and applications see, for example, Refs. 47 and 101-106). According to the literature relying on the BO paradigm, there are bound rotation(-vibration) energy levels corresponding to the  $X^1\Sigma_g^+$ ,  $B^1\Sigma_u^+$ , and  $a^3\Sigma_g^+$ , while the  $b^3\Sigma_u^+$  electronic state is repulsive.

In our calculations, we obtained rotation energy levels lower than the corresponding dissociation thresholds in cases (1), (3), and (4) assignable to  $X^1\Sigma_g^+$ ,  $B^1\Sigma_u^+$ , and  $a^3\Sigma_g^+$  electronic states, respectively. Whereas in case (2) the calculated energy levels converged from above to the energy of two ground-state hydrogen atoms,  $E(\text{H}(n=1) + \text{H}(n=1))$  (see Table IV), in agreement with the known results based on the BO theory.<sup>100</sup>

Although the lowest-lying dissociation products are two ground-state hydrogen atoms,  $\text{H}(n=1) + \text{H}(n=1)$  with  $E(\text{H}(n=1) + \text{H}(n=1)) = -0.499727840 E_h$ , the rotation-vibration-electronic wave function can have different symmetry properties upon the interchange of identical particles, which can correspond to higher-lying dissociation thresholds. Although these states have larger energies than the dissociation continuum of the two ground-state hydrogen atoms, they can be calculated within our variational procedure because of their different symmetry (and different spin). Concerning the

TABLE IV. Calculated energy levels of  $H_2 = \{p^+, p^+, e^-, e^-\}$ .

$L^a$	$p^a$	$S_p^a$	$S_e^a$	$E/E_h^b$	$\eta^c$	$\delta E/\mu E_h^d$	Ref.	Assignment <sup>e</sup>		
0	1	0	0	-1.164025026	$1.4 \times 10^{-8}$	-0.004	62, 63	para	singlet	$X^1\Sigma_g^+$
1	-1	1	0	-1.163485167	$3.2 \times 10^{-9}$	-0.006	47	ortho	singlet	$X^1\Sigma_g^+$
2	1	0	0	-1.162410402	$2.2 \times 10^{-8}$	-0.007	47	para	singlet	$X^1\Sigma_g^+$
3	-1	1	0	-1.160810486	$7.9 \times 10^{-9}$	-0.006	47	ortho	singlet	$X^1\Sigma_g^+$
4	1	0	0	-1.158699660	$6.7 \times 10^{-9}$	-0.006	47	para	singlet	$X^1\Sigma_g^+$
[...]										
0	1	1	1	[-0.999450]	$[6.3 \times 10^{-6}]$	[-5.8]	100	ortho	triplet	$b^3\Sigma_u^+$
1	-1	0	1	[-0.999445]	$[8.9 \times 10^{-6}]$	[-10.4]	100	para	triplet	$b^3\Sigma_u^+$
[...]										
0	1	1	0	-0.753026938	$1.8 \times 10^{-6}$	-0.455	106	ortho	singlet	$B^1\Sigma_u^+$
1	-1	0	0	-0.752848338	$5.9 \times 10^{-6}$	-2.041	106	para	singlet	$B^1\Sigma_u^+$
[...]										
0	1	0	1	-0.730825002	$1.2 \times 10^{-6}$	-0.198	108	para	triplet	$a^3\Sigma_g^+$
1	-1	1	1	-0.730521133	$7.4 \times 10^{-7}$	-0.277	108	ortho	triplet	$a^3\Sigma_g^+$
[...]										

<sup>a</sup> $L$ : quantum number of the total angular momentum without the spins;  $p$ : parity;  $S_p$ : total spin quantum number of the protons;  $S_e$ : total spin quantum number of the electrons.

<sup>b</sup> $m_p/m_e = 1836.15267247$ .<sup>86</sup> The energy of the lowest-lying dissociation threshold is  $E(H(n=1) + H(n=1)) = -0.999455679 E_h$ , while the third and fourth set of states belong to a different symmetry block, and the corresponding dissociation threshold is  $E(H(n=1) + H(n=2)) = -0.624659800 E_h$ . The wave function for the  $X^1\Sigma_g^+$  (for the  $B^1\Sigma_u^+$ ,  $a^3\Sigma_g^+$ ) states was written in terms of a linear combination of  $N_b = 1500$  ( $N_b = 1000$ ) basis functions and the  $K$  values of the “2K” exponents of the polynomial prefactors were generated in a normal distribution with mean and variance 9 and 1, respectively, and the generated value was rounded to the nearest integer.

<sup>c</sup> $\eta = |1 + \langle \Psi | \hat{V} | \Psi \rangle / (2 \langle \Psi | \hat{T} | \Psi \rangle)|$ .

<sup>d</sup> $\delta E = E(\text{Ref.}) - E$ .

<sup>e</sup>The para (ortho) and singlet (triplet) descriptions correspond to  $S_p = 0$  (1) and  $S_e = 0$  (1), respectively. The electronic-state label of the Born–Oppenheimer theory is assigned to the calculated energy levels based on comparison with the literature.<sup>47, 100, 106, 108</sup> In each case, the vibrational ground state is shown, i.e., the lowest energy level corresponding to each set of angular momentum, parity, and spin quantum numbers.

clamped-nucleus analogy, correlation rules between molecular states and dissociation limits were derived by Hund<sup>110, 111</sup> and by Wigner and Witmer<sup>112</sup> for homonuclear diatomic molecules, which were later extended by Mulliken<sup>113</sup> (see also Refs. 109 and 114).

As to the technical details of our calculations, we used LF Cartesian coordinates to optimize the logarithm of the basis function exponents,  $\ln \alpha_{ij}$ , while the GVR coefficients were generated first corresponding to the atoms-in-molecule coordinates<sup>85</sup> (see “AIM- $H_2$ ” in Figure 6). The random number generators were parameterized following the sampling-importance-resampling strategy for the  $X^1\Sigma_g^+$  states. These random distributions (normal distributions with some mean and variance for each  $\ln \alpha_{ij}$  ( $i = 1, 2, \dots, n_p + 1$ ;  $j = i + 1, \dots, n_p + 1$ ) and  $u_i^{(\text{AIM}-H_2)}$  ( $i = 1, 2, \dots, n_p$ )) were used not only for the  $X^1\Sigma_g^+$  states but also for the generation of the trial parameters for the electronically excited states. Of course, the internal distribution of the particles can be very different in the various electronic states, as it can be anticipated from the very different minimum positions and width of the potential energy curves (Figure 8). Thus, if we reparameterized the random distributions of the random number generators for each electronically excited state (following a sampling-importance-resampling strategy), we could have a more efficient optimization procedure, and thus could calculate lower energy eigenvalues with a similar computational effort. This requires a series of calculations, which we might pursue in a later work.

As to the optimization of the global vector coefficients, the parameter optimization in terms of the AIM coordinates seem to represent the physical idea that the lighter electrons “follow” the heavier protons, and thus provide a rea-

sonable choice for the parameterization of the angular distribution of the particles. Of course, the coordinates of the two electrons and the two protons enter the procedure symmetrically due to the (anti)symmetrization of the trial functions, Eq. (10).

In Table IV, we present the calculated energy values and their comparison with earlier calculations. For  $L = 0$ ,  $S_p = 0$ ,  $S_e = 0$  tightly converged all-particle (“pre-Born–Oppenheimer”) variational calculations<sup>62, 63</sup> were used as reference data. For every other energy levels calculations within a pre-Born–Oppenheimer approach were not available, and we compared our results to the results of accurate “post-Born–Oppenheimer” variational-perturbational calculations.<sup>47, 101–106</sup> The  $b^3\Sigma_u^+$  energy eigenvalues shown in Table IV converged from above to the energy of two ground-state hydrogen atoms, which we interpret as an indication of the repulsive character of this electronic state in the BO theory.

Although the numerical results reported in Table IV could be improved, our goal is accomplished by demonstrating that rotational energy levels corresponding to the ground and some excited energy levels can be calculated within the presented variational all-particle procedure.

As a next logical question, one may ask if it is possible to calculate rotation(-vibration) energy levels corresponding to higher-lying bound electronic states, for example, to  $e^3\Sigma_u^+$ ,<sup>109</sup> within the present approach. We think that the rotation(-vibration) states, which could be assigned to  $e^3\Sigma_u^+$ ,<sup>109</sup> are embedded in the continuum assignable to the  $b^3\Sigma_u^+$ , and thus could be calculated as resonances with some characteristic energy and finite lifetime within an all-particle approach.

TABLE V. Calculated energy levels of  ${}^7\text{Li} = \{{}^7\text{Li}^{3+}, e^-, e^-, e^-\}$ .

$L^a$	$p^a$	$S_e^a$	$E^b$	$\eta^c$	$\delta E/\mu E_h^d$	Ref.
0	1	1/2	-7.477451901	$1.3 \times 10^{-9}$	-0.029	115
1	-1	1/2	-7.409557349	$8.8 \times 10^{-9}$	-0.410	116
2	1	1/2	-7.334926959	$1.1 \times 10^{-9}$	-0.347	117, 118

<sup>a</sup> $L$ : quantum number of the total angular momentum without the spins;  $p$ : parity;  $S_e$ : total spin quantum number of the electrons.

<sup>b</sup> $m_{7\text{Li}^{3+}}/m_{e^-} = 12\,786.393$  The wave functions were optimized as a linear combination of  $N_b = 1500$  basis functions and the exponents of the polynomial prefactors were  $2K = 0$  or  $2$ , selected randomly.

<sup>c</sup> $\eta = |1 + \langle \Psi | \hat{V} | \Psi \rangle / (2 \langle \Psi | \hat{T} | \Psi \rangle)|$ .

<sup>d</sup> $\delta E = E(\text{Ref.}) - E$ .

## D. ${}^7\text{Li}$

The last system to be considered is the  ${}^7\text{Li}$  isotopologue of the lithium atom described as a four-particle quantum system with three spin-1/2 fermionic particles (electrons). The numerical results obtained for the doublet electronic states are collected in Table V and agree well with the available literature data.<sup>115–118</sup>

## E. On the transferability of optimized basis function parameters

We should describe our observations concerning the transferability of the non-linear parameters of the basis functions. Assume that there is a set of basis function parameters,  $\mathcal{B}(A)$ , optimized for some system  $A$ , where  $A$  is a collective symbol for the input parameters of a calculation (mass, charge, and spin of the particles, quantum numbers, size of the basis set, etc.). Then, we use  $\mathcal{B}(A)$  to parameterize the basis functions for calculation  $A'$  (with particles of some mass, charge, and spin, quantum numbers, etc.) and solve the linear variational problem only

$$\Psi^{(A')} = \sum_{I=1}^{N_b} c_I \Phi_I^{(A')}[\mathcal{B}_I(A)] \quad (63)$$

to obtain an estimate (an upper bound),  $E^{(A')}[\mathcal{B}(A)]$  to the energy for  $A'$ . We may say that the basis function parameters are transferable from calculation  $A$  to  $A'$  if the energy estimate

$E^{(A')}[\mathcal{B}(A)]$  is close to the energy obtained with optimizing the basis function parameters for system  $A'$ ,  $E^{(A')}[\mathcal{B}(A')]$ .

We emphasize here that we do not transfer the basis functions but only the parameters (geminal exponents, global vector coefficients, polynomial exponents), while the mathematical form of the basis functions is determined by the quantum numbers (spatial and permutational symmetries). This strategy is reminiscent of the vibrational subspace technique for an efficient calculation of rotation-vibration energy levels<sup>119</sup> using pre-calculated vibrational wave functions.

In Table VI, we present examples for such a transfer of the basis function parameters between rotational energy levels of  $\text{H}_2$  ( $X^1\Sigma_g^+$  electronic state) with various  $L$  quantum numbers. In this example, the basis function parameters optimized for a rotational energy level of  $\text{H}_2$  with  $L'$  were used for the parameterization of basis functions for another rotational energy level with  $L$ . Table VI shows that the parameterization transfer between neighboring rotational energy levels,  $L = L' \pm 1$ , gives an estimate within  $0.5 \mu E_h$  of the optimized value. For larger  $|L - L'|$  values, the solution of the linear variational problem only seems to provide less and less good estimates. A qualitative explanation for this observation can be given as follows. For neighboring rotational states, the internal distribution of the particles is similar, and thus the same parameter set can describe both states, while the mathematical form of the basis functions is determined by the quantum numbers, and the flexibility of this ansatz is provided by the linear variational coefficients.

## IV. SUMMARY AND OUTLOOK

The variational solution of the Schrödinger equation of few-particle systems was considered without the introduction of the Born–Oppenheimer approximation. We presented an algorithm and reported some numerical results calculated with a computer program (implemented in FORTRAN 90), which are based on (a) a quantum Hamiltonian expressed in terms of laboratory-fixed or translationally invariant Cartesian coordinates; (b) basis functions constructed with symmetry-adapted explicitly correlated Gaussian functions and polynomial prefactors also using the global vector

TABLE VI. On the transferability of the basis function parameters between different rotational levels of  $\text{H}_2$  corresponding to the  $X^1\Sigma_g^+$  electronic state (see also Table IV). The energy differences,  $\Delta E_L[\mathcal{B}(L')]$ , between the energy obtained via the optimization of the basis function parameters,  $\mathcal{B}(L)$  and four transferred parameter sets,  $\mathcal{B}(L')$ , are given in  $\mu E_h$ .

$L^a$	$E_L[\mathcal{B}(L)]/\mu E_h^{b,c}$	$\Delta E_L[\mathcal{B}(0)]^{b,d}$	$\Delta E_L[\mathcal{B}(1)]^{b,d}$	$\Delta E_L[\mathcal{B}(2)]^{b,d}$	$\Delta E_L[\mathcal{B}(3)]^{b,d}$	$\Delta E_L[\mathcal{B}(4)]^{b,d}$
0	-1.164025026	0.00	-0.06	-1.53	-2.53	-5.03
1	-1.163485167	-0.21	0.00	-0.35	-0.97	-2.54
2	-1.162410402	-0.76	-0.09	0.00	-0.21	-1.01
3	-1.160810486	-1.53	-0.37	-0.29	0.00	-0.23
4	-1.158699660	-2.41	-0.83	-1.05	-0.18	0.00

<sup>a</sup> $L$ : quantum number of the total angular momentum without the spins;  $p = (-1)^L$ : parity;  $S_e = 0$ ; and  $S_p = (1 - p)/2$ . See also the entries of Table IV assigned to the Born–Oppenheimer electronic ground state,  $X^1\Sigma_g^+$ .

<sup>b</sup>The mass ratio is  $m_p/m_e = 1836.15267247$ .

<sup>c</sup> $E_L[\mathcal{B}(L)]$  is the lowest eigenvalue obtained in the non-linear variational optimization, and the optimized basis function parameters are  $\mathcal{B}(L)$ .

<sup>d</sup> $\Delta E_L[\mathcal{B}(L')] = E_L[\mathcal{B}(L)] - E_L[\mathcal{B}(L')]$  ( $L' = 0, 1, 2, 3, 4$ ), where  $E_L[\mathcal{B}(L')]$  is the lowest eigenvalue of the linear variational problem solved for a set of basis functions parameterized with  $\mathcal{B}(L')$ , which was optimized for the angular momentum quantum number ( $L'$ ).

representation;<sup>59</sup> (c) analytic expressions for the calculation of the overlap, the kinetic, and the potential energy integrals following the prescriptions of Refs. 35 and 53; and (d) stochastic variational optimization of the non-linear parameters of the basis functions.

Our work is a practical adaptation of that described in Refs. 35 and 53 for molecular systems with various (rotational or orbital) angular momentum quantum numbers ( $L \geq 0$ ). An accurate calculation of the energy levels of molecular systems required the inclusion of large exponents ( $>4$ ) for the polynomial prefactors in the basis functions. In order to obtain a numerically stable and practical implementation with large exponents, we had to rearrange the integral expressions of Refs. 35 and 53, introduce quasi-normalization for the basis functions, use a logarithmic evaluation of products of polynomials and factorials, and pursue a careful implementation strategy.

It was an advantageous property of the basis functions that upon a linear transformation of the Cartesian coordinates their mathematical form remained unaltered, and only the basis function parameters (Gaussian exponents and global vector coefficients) had to be transformed. We did make use of this simple transformation property during the integral evaluation and the parameter optimization. During the evaluation of the integrals the operators were written in their simplest form in terms of the coordinates.

Clearly, we had to *choose* some set of coordinates for the parameter optimization, but we were able to exploit the ease of re-parameterization of the basis functions in terms of different coordinates. For the systems studied here, we have found the best to generate and optimize the Gaussian exponents corresponding to laboratory-fixed Cartesian coordinates, while for the global vector coefficients some “well-chosen” translationally invariant Cartesian coordinates performed better.

In general, it is not trivial how to choose an appropriate set of coordinates or there might be not only one but several types of correlations in the system, which are represented efficiently by different sets of coordinates. To circumvent this coordinate dilemma, we suggested a multiple-channel optimization strategy for the optimization of the basis function parameters. Indeed, due to the simple transformation property of the basis functions upon a linear transformation of the coordinates, the basis function parameters can be optimized in terms of one or another set of the coordinates during the course of the *same* calculation.

Besides the stochastic optimization (competitive selection and refinement<sup>35</sup>) of the non-linear parameters, we included repeated fine-tuning cycles. In the stochastic optimization procedure, we studied the effect of various random number generators on the efficiency of the procedure, i.e., the convergence rate of the energy with respect to the computational effort, and finally selected a log-normal distribution for each Gaussian exponent and normal distributions for the global vector coefficients. We have proposed a sampling-importance-resampling strategy for the parameterization of the random number distribution, i.e., to be able to choose a reasonably good sample mean and sample variance for the probability distributions.

Our emphasis was on the calculation of energy levels and wave functions with *various* quantum numbers of total spatial angular momentum (rotational and orbital angular momenta of the BO theory), parity, and spin quantum numbers. Though in this work we restricted the presentation to the natural-parity case,  $p = (-1)^L$  only, we have preliminary results for the unnatural parity case,  $p = (-1)^{L+1}$  as well, which might be presented in a later publication.

Although the optimization, especially the “fine-tuning” of the basis function parameters could be certainly improved, our primary goal was here to test the applicability of the procedure, and thus we calculated rotation-vibration energy levels of the molecular  $\text{H}_2^+$  corresponding to the  $\tilde{X}^2\Sigma_g^+$  ground and the  $\tilde{A}^2\Sigma_u^+$  electronically excited states as well as rotational energy levels of  $\text{H}_2$  assigned to the  $X^1\Sigma_g^+$  ground and to the  $B^1\Sigma_u^+$  and  $a^3\Sigma_g^+$  electronically excited states. We also calculated three bound states of the positronium molecule,  $\text{Ps}_2$ , and the  $^7\text{Li}$  atom with various angular momentum quantum numbers.

The assignment of the calculated energy levels to electronic states defined within the Born–Oppenheimer theory was carried out based on the comparison of the calculated energy eigenvalues with the literature. It would be possible to make the assignment based on the analysis of the calculated wave function, which can be explored in a later work. The development of such an assignment tool would allow us to better understand the qualitative meaning of the parameterization of the wave function, and thus could help the improvement of the parameterization strategy and a development of a systematic approximation scheme.

For future work, it would be interesting to calculate rotation-vibration energy levels, for example, for the  $\text{H}_2$  molecule, which can be assigned to higher-lying electronically excited states of the Born–Oppenheimer theory. This undertaking appears not to be a simple, straightforward task in the present all-particle quantum mechanical approach. We believe that these states could be calculated as resonances embedded in the continuum of lower-lying energy levels of the same symmetry.

Finally, we discussed the transferability of the basis function parameters between rotational states of the  $\text{H}_2$  molecule. We have found that between neighboring rotational levels the transferred parameters provided a satisfactory basis set, which—without further optimization of the non-linear parameters—, when used in a linear variational problem to parameterize the basis functions corresponding to the actual quantum numbers, provided a very good approximation to the energy.

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