Generalized elimination of the global translation from explicitly correlated Gaussian functions

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Abstract

This paper presents the multi-channel generalization of the center-of-mass kinetic energy elimination approach [Mol. Phys., 111 2086 (2013)] when the Schrödinger equation is solved variationally with explicitly correlated Gaussian functions. The approach has immediate relevance in many-particle systems which are handled without the Born–Oppenheimer approximation and can be employed also for Dirac-type Hamiltonians. The practical realization and numerical properties of solving the Schrödinger equation in laboratory-frame Cartesian coordinates are demonstrated for the ground rovibronic state of the H⁺ = {p⁺, p⁺, e⁺} ion and the H₂ = {p⁺, p⁺, e⁺, e⁺} molecule.

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I. INTRODUCTION

Explicitly correlated Gaussian (ECG) functions have a long history in variational calculations of few-particle quantum mechanical systems [1–7] yielding results with a nano-Hartree accuracy in the energy. An obvious advantage of these functions is that analytic matrix elements can be derived for almost all physically relevant operators and for an arbitrary number of particles. This general applicability is a particularly important advantage for our work, in which we aim to develop a general approach for atoms, molecules, or other more exotic molecular “objects” (e.g., positronium complexes) by considering all particles on equal footing, i.e., without introducing the Born–Oppenheimer (BO) approximation. We refer to this framework as a pre-Born–Oppenheimer (pre-BO) theory in order to emphasize the departure from the traditional (and undoubtedly very successful) Born–Oppenheimer approximation and other “post-Born–Oppenheimer” approaches, which correct for or go beyond the BO approximation.

The spatial symmetry properties of the pre-BO approach are reminiscent of nuclear motion theory (or also called “quantum dynamics”) in which the rovibrational Schrödinger equation is solved on some potential energy surface. In both cases, the full Hamiltonian has a continuous spectrum due to the overall translation of the system. In order to obtain the translation-free, i.e., translationally invariant, properties, the laboratory-frame Cartesian coordinates (LFCC) are traditionally replaced by a translationally invariant set of Cartesian coordinates (TICC) and the Cartesian coordinates of the center of mass (CMCC). This linear transformation [8]—although rather simple in comparison to the commonly introduced body-fixed frame, orientational angles, and curvilinear internal coordinates to efficiently describe rotating-vibrating molecular systems [9–12]—makes the original, very simple Cartesian kinetic energy operator more complicated. Certainly, the resulting TICC kinetic energy operator (after subtracting the center-of-mass kinetic energy term) has been successfully used many times, see for example [6, 7, 13–16], it is also reasonable to ask whether it is possible to avoid any coordinate change at all and stay with the original, mathematically and conceptually very simple laboratory-fixed Cartesian coordinates. One might ask why to look for an alternative to the already working TICC approach—we ask: why not? To give a historical example in which similar questions resulted in important developments, we mention the numerical evaluation of the diagonal Born–Oppenheimer correction (DBOC)
(within the post-BO framework). The calculation of the DBOC has been made extremely
elegant and simple by Handy and co-workers \cite{17,20} by using laboratory-fixed Cartesian
coordinates, instead of the earlier used more tedious way of choosing some TICC set and
transforming the relevant expressions to this TICC and CMCC coordinate set.

Back to our pre-BO framework, Ref. \cite{21} has shown that it is possible to calculate the
translation-free part of the spectrum, i.e., rotational-vibrational-electronic levels, of any iso-
lated many-particle system by solving the Schrödinger equation in laboratory-frame Carte-
sian coordinates. In this approach, the CM kinetic energy contribution is cancelled during
the integral evaluation of the ECG basis functions.

Although the integral evaluation with ECGs is straightforward, their parameterization—
which is after all a very high-dimensional parameterization problem—requires special care in
particular when highly accurate energy levels of molecular systems (i.e., assemblies of light
and heavy particles) are to be calculated. The LFCC approach of Ref. \cite{21} was developed
for a certain way of parameterization. The present work generalizes this LFCC approach
and makes it applicable together with the most general “multi-channel optimization” of the
ECG parameter set, in which the optimization approach cycles through various pairs of
particles and groups of particles and varies the ECG parameters (exponents) to describe the
interaction of these pairs or groups optimally.

To this end, we had to study in detail the general properties of the LF→(TI,CM) Carte-
sian coordinate transformation, as well as the analytic kinetic energy expectation value
expressions, which is described in the first part of the article. In the second part, we
demonstrate the general applicability of this generalized LFCC approach and the excellent
numerical and convergence properties of the multi-channel optimization. As “relativistic
effects” have been shown to be equally important to “nonadiabatic effects” in light systems,
see for example Ref. \cite{22}, we emphasize that the LFCC approach developed in the present
paper is transferable to the Dirac theory which we will consider in future work.

II. THE SCHRÖDINGER HAMILTONIAN AND COORDINATE SETS

Given a collection of Cartesian coordinates let us consider the laboratory-frame (LF) Carte-
sian coordinates, \( \mathbf{r} = (\mathbf{r}_1, \ldots, \mathbf{r}_{N_p})^T \), of \( N_p \) particles associated with some \( m_i \) masses and \( q_i \)electric charges, which parameterize the instantaneous Coulomb interactions acting among
the particles. The Schrödinger Hamiltonian, in Hartree atomic units is

$$\hat{H}_S = -\nabla^T r M \nabla r + \sum_{i=1}^{N_p} \sum_{j>i}^{N_p} \frac{q_i q_j}{|r_i - r_j|}. \quad (1)$$

where $\nabla r = (\nabla_{r_1}, \ldots, \nabla_{r_{N_p}})^T$ collects the 3-dimensional Nabla operators for each particle and the diagonal $M_{ij} = \delta_{ij} \frac{1}{2m_i}$ matrix, which absorbs the $\frac{1}{2}$ term to shorten later notation.

Then, we consider a linear transformation of the coordinates:

$$U_x r = (x_1, x_2, \ldots, x_{N_p-1}, x_{CM})^T \quad (2)$$

in which the $x_{CM} = \sum_{i=1}^{N_p} m_i r_i / (\sum_{i=1}^{N_p} m_i)$ center-of-mass Cartesian coordinates (CMCC) are introduced and $(x_1, \ldots, x_{N_p-1})$ labels the translationally invariant Cartesian coordinates (TICC) corresponding to $U_x$. Any transformation matrix $U_x$ can be selected which satisfy the translational invariance and the center-of-mass translational conditions:

$$\sum_{j=1}^{N_p} (U_x)_{ij} = 0 \quad \text{with} \quad i \in \{1, \ldots, N_p - 1\}, \quad (3)$$

and

$$(U_x)_{N_p,j} = \frac{m_j}{m_1 \ldots m_{N_p}} \quad (4)$$

respectively, and $m_{j \ldots k} = \sum_{i=j}^{k} m_i$.

There are infinitely many possible linear transformations which satisfy Eqs. (3)–(4) among which there are a few more common ones (Fig. 1 visualizes three examples). In the present work, we shall use Jacobi coordinates,

$$x^{Jac}_i = \sum_{j=1}^{i} \frac{m_j}{m_{1 \ldots i}} r_j - r_{i+1}, \quad (5)$$

the heavy-particle centered (HPC) coordinates (where the “heavy particle”, $r_{HP}$, is arbitrarily selected from the heavy particles)

$$x^{HPC}_i = r_i - r_{HP}, \quad (6)$$

and the center-of-mass-centered (CMC) coordinates

$$x^{CMC}_i = r_i - \sum_{j=1}^{N_p} \frac{m_j}{m_{i \ldots N_p}} r_j. \quad (7)$$
Upon the transformation $r \rightarrow (x_1, x_2, \ldots, x_{CM})$ the operators change as follows:

$$\nabla_r \rightarrow \left( \nabla_{x_1}, \ldots, \nabla_{x_{Np-1}}, \nabla_{x_{CM}} \right)$$

(8)

where $(\nabla_{x_i}) = \frac{\partial}{\partial x_{ia}}$ ($a = x, y, z$) and

$$\hat{T} = -\frac{1}{2m_{1\ldots Np}} \nabla^2_{x_{CM}} - \nabla^T_{x} \mu \nabla_{x}$$

(9)

Accordingly the mass matrix changes to (see also Sec. [IV]),

$$U_x^{-T} M U_x^{-1} = \begin{bmatrix} \mu & 0 \\ 0 & \frac{1}{2m_{1\ldots Np}} \end{bmatrix}.$$

(10)

III. EXPLICITLY CORRELATED GAUSSIAN FUNCTIONS

Let us consider the family of square-integrable, positive definite functions

$$\phi_I (r; \{\omega_I\}) : \mathbb{R}^{3Np} \rightarrow \mathbb{R}$$

(11)

with $\{\omega_I\}$ parameters and dim $\{\omega_I\} \geq 1$. We always choose $\omega_{I,1} = A^{(q)}$, with a real $(3Np \times 3Np)$ $A^{(q)}$ matrix of scalar values defined as

$$A^{(q)} = \bar{A}^{(q)} \otimes I_3.$$

(12)

The superscript $q \in \{r, x, y, \ldots\}$ labels the coordinate set: $q = r$ indicates that the matrix is expressed in LFCC, otherwise $q = x, y, \ldots$ refers to a certain TICC selection. The function
\( \phi_I \) keeps its mathematical form during the course of the coordinate transformation and is parameterized with some \( \{ \omega_I \} \) set. Upon a linear transformation \( r \rightarrow x \), described by the matrix \( U_x \), Eqs. (2)–(4), the parameter set \( \{ \omega_I \} \) is also transformed as

\[
\bar{A}^{(x)} = U_x^{-T} \bar{A}^{(r)} U_x^{-1}
\]

(13)

with

\[
\bar{A}^{(x)} = \begin{bmatrix} A^{(x)} & 0 \\ 0 & c_A \end{bmatrix}
\]

(14)

where the \( A^{(x)} \in \mathbb{R}^{(N_p-1) \times (N_p-1)} \) matrix corresponds to the selected TICC and \( c_A \) is the only parameter related to the center-of-mass coordinates.

Using this family of functions, we approximate the exact eigenfunction of the Schrödinger equation with a linear combination of \( N_b \) properly (anti)symmetrized products of \( \phi_I \) spatial and \( X^{S,M_S}_I \) spin functions:

\[
\Psi(r) = \sum_{I=1}^{N_b} c_I X^{S,M_S}_I \hat{Y} \phi_I(r; \{ \omega_I \})
\]

(15)

where the \( c_I \)'s are the linear combination coefficients and \( \hat{Y} \) is the Young operator projecting onto the appropriate (anti)symmetric subspace.

In this work, we shall consider three types of ECG functions for the \( \phi_I \) spatial basis function. These functions are introduced in the following subsections.

A. Plain Explicitly correlated Gaussian functions (pECGs)

The plain ECG functions (pECGs) are the simplest representatives of ECG-type functions:

\[
\phi_I^{\text{pECG}}(r; A^{(r)}_I) = \exp \left[ -\frac{1}{2} r^T A^{(r)}_I r \right].
\]

(16)

They are eigenfunctions of the square of the total angular momentum operator, \( \hat{N}^2 \), with \( N = 0 \) quantum number and they are parity eigenstates with \( p = +1 \). The pECGs have simple analytic integral expressions for the most important operators.
B. Floating explicitly correlated Gaussian functions (FECGs)

A more flexible functional form is introduced by allowing shifted particle positions \((\mathbf{r} - \mathbf{s}_I)\)—hence the name floating ECG (FECG) functions—defined as:

\[
\phi_i^{\text{FECG}}(\mathbf{r}; A_i^{(r)}, \mathbf{s}_i^{(r)}) = \exp \left[ - \left( \mathbf{r} - \mathbf{s}_i^{(r)} \right)^T A_i^{(r)} \left( \mathbf{r} - \mathbf{s}_i^{(r)} \right) \right] = \exp \left[ -\mathbf{s}_i^{(r)^T} A_i^{(r)} \mathbf{s}_i^{(r)} - \mathbf{r}^T A_i^{(r)} \mathbf{r} + 2 \mathbf{r}^T A_i^{(r)} \mathbf{s}_i^{(r)} \right].
\]

(17)

For non-vanishing \(s_i^{(r)}\) shift vectors, the FECGs are generally neither eigenfunctions of the total angular momentum operators, \(\hat{N}_2^2\) and \(\hat{N}_z\), nor eigenfunctions of the space-inversion operator. Therefore, FECGs are usually considered to be less appropriate for approximating spherically symmetric states than pECGs. At the same time, they are better suited for describing less delocalized particles (e.g., atomic nuclei) due to the more flexible parameterization. In a variational computation, the spherical symmetry is restored numerically by variationally optimizing basis sets of increasing size.

C. Explicitly correlated Gaussian functions with global vector representation (ECGs-GVR)

The ideal basis functions are eigenfunctions of the spatial symmetry operators \((\hat{N}_2^2, \hat{N}_z\) and parity) and they are sufficiently flexible in their parameterization to account for very different types of particle distributions.

The pECG functions can be made eigenfunctions of \(\hat{N}_2^2\) by multiplying it with an angular factor \(\tilde{\theta}_{NMN}(\mathbf{r})\) defined as a vector-coupled product of solid spherical harmonics \(\mathcal{Y}_l(\mathbf{r}_i)\) of particle \(i\)

\[
\tilde{\theta}_{NMN}(\mathbf{r}) = \left[ \left[ [\mathcal{Y}_{l_1}(\mathbf{r}_1)\mathcal{Y}_{l_2}(\mathbf{r}_2)]_{N_{12}} \mathcal{Y}_{l_3}(\mathbf{x}_3) \right]_{N_{123}} \ldots \right]_{NMN}.
\]

(18)

The subsystems’ angular momenta, \(l_1, l_2, \ldots, N_{12}, N_{123}, \ldots\) are not conserved and for a realistic description of few-body problems one must include several \((l_1, l_2, \ldots, l_N; N_{12}, N_{123}, \ldots)\) sets. The various possible partial wave contributions from each set increase both the basis set dimension and the complexity of the integrals associated with expectation values of quantum mechanical operators. Moreover, the change of \(\tilde{\theta}_{NMN}(\mathbf{r})\) upon changing the coordinate set usually leads to very complicated expressions.
An alternative to this commonly used vector-coupled form has been proposed by Suzuki and Varga [23, 24]:

$$\theta_{NM_N} (r; u^{(r)}, K) = |v^{(r)}|^{2K+L} Y_{NM_N}$$  \hspace{1cm} (19)

with the global vector $v \equiv \sum_{i=1}^{N} u_i r_i = \tilde{u}^{(r)} r$ being a linear combination of all (pseudo-)particle coordinates. It has been shown that when used in a variational procedure the pECGs multiplied with either Eq. (18) or (19) result in a mathematically equivalent representation. In Eq. (19) only the conserved total orbital angular momentum quantum number, $N$, appears, whereas the explicit coupling of the subsystems’ angular momenta is completely avoided (it is implicitly carried by the global vectors in the variational ansatz). The coefficients $u_i$ in the global vector are variational parameters to be optimized by minimizing the energy. Upon the transformation of the coordinates, Eq. (2)–(4), the vector $u \in \mathbb{R}^{N_p}$ transforms as

$$U^{-T}_x u^{(r)} = \left( \begin{array}{c} u' \\ c_U \end{array} \right),$$  \hspace{1cm} (20)

The $K$ integer parameter in Eq. (19) introduces additional variational flexibility for the basis function (qualitatively, it helps to describe more efficiently localized, vibrating atomic nuclei).

In the so-called global vector representation (GVR) the angular term in Eq. (19) multiplies a pECG:

$$\phi_{ECG-GVR}^{NM_N} (r; A^{(r)}_I, u^{(r)}_I, K_I) = \theta_{NM_N} (r; u^{(r)}, K_I) \cdot \exp \left[ -\frac{1}{2} r^T A^{(r)}_I r \right].\hspace{1cm} (21)$$

This choice of the basis functions leads to compact $N_p$-particle analytic integrals for the most important physical operators and corresponds to well-defined values for the spatial quantum numbers (total angular momentum, $N$ and $M_N$, and parity).

IV. IDENTIFICATION OF THE GLOBAL TRANSLATIONAL CONTRIBUTIONS IN AN LFCC CALCULATION

In this section we study the analytic integrals of the overlap and the Schrödinger Hamiltonian expressed in the original laboratory-frame Cartesian coordinates (LFCC) in order to identify the translationally-invariant terms and eliminate others, which originate from the overall translation of the system.
Most importantly, we rely on the invariance of the functional form of all ECG-type functions considered in this work, upon a linear transformation, and in particular the Eq. (2)–(4) transformation, of the coordinates. The mathematical form of the functions is unchanged, while the parameters transform as follows:

$$\phi_{ECG}^{(r)}(r \rightarrow U_x^{-1} x; A_I^{(r)}) = \exp \left[ -\frac{1}{2} (U_x^{-1} x)^T A_I^{(r)} (U_x^{-1} x) \right]$$

$$= \exp \left[ -\frac{1}{2} x^T (U_x^{-T} A_I^{(r)} U_x^{-1} \otimes I_3) x \right]$$

$$= \exp \left[ -\frac{1}{2} x^T A_I^{(x)} x \right] = \phi_{ECG}(x; A_I^{(x)}). \quad (22)$$

Conceptually, a special parameterization of the basis functions allows for the detection and removal of CM translational contributions at the level of the kinetic energy expectation value. In our earlier work [21], we have pointed out that a few controllable CM-dependent terms and factors can be identified in the (kinetic energy) integral expressions. These terms were eliminated during the course of the integral evaluation in order to obtain translation-free values.

Ref. [21] focused on ECG-GVR functions in which the variational parameter matrix $A_I$ and the global vector $u_I$ was transformed back and forth between different coordinate representations according to

$$A_I^{(r)} = U_x^T A_I^{(x)} U_x \quad \iff \quad A_I^{(x)} = U_x^{-T} A_I^{(r)} U_x^{-1}, \quad (23)$$

and

$$u_I^{(r)} = U_x^T u_I^{(x)} \quad \iff \quad u_I^{(x)} = U_x^{-T} u_I^{(r)} \quad (24)$$

where $U_x$ satisfies the translational invariance and CM conditions, Eqs. (3) and (4), respectively.

When expressed with some TICC (and CMCC) $A_I$ and $u_I$ have the special block structure:

$$A_I^{(x)} = \begin{pmatrix} A_I^{(x)} & 0 \\ 0 & c_A \end{pmatrix} \quad \text{and} \quad u_I^{(x)} = \begin{pmatrix} u_I^{(x)} \\ c_U \end{pmatrix}. \quad (25)$$

Since $c_A$ and $c_U$ are related to the CM coordinates, $x_{CM}$, the system is “at rest” only for $c_A = 0$ and $c_U = 0$. Although $c_U$ can be set to zero without any problems, if $c_A$ was chosen to be zero, the $A$ matrix would become singular, which violates the square integrable and positive definiteness requirements for the basis functions.
Ref. [21] defined the following approach to handle the $c_A$-dependent terms without violating the square-integrability and positive-definiteness conditions:

1. For each basis function $I$, generate, optimize, or read in the $(\bar{A}_I^{(x)})_{ij}$ values with $i, j \in \{1, \ldots, N_b\}$.

2. Construct the elements of the exponent matrix in the LFCC framework as

$$
(\bar{A}_I^{(r)})_{ij} = -(\bar{A}_I^{(x)})_{ij} (1 - \delta_{ij}) + \left( \sum_{k=1, k\neq i}^{N_p} (\bar{A}_I^{(x)})_{ij} \right) \delta_{ij} + c_A \frac{m_i}{m_{1\ldots N_p}} \frac{m_j}{m_{1\ldots N_p}}
$$

with $i, j = 1, \ldots, N_p$ and some $c_A > 0$ value.

3. For $c_A > 0$ the matrices $\bar{A}_I^{(r)}$ are non-singular, $|\bar{A}_I^{(r)}|$ and also $\bar{A}_I^{(r)-1}$ can be evaluated. At the same time, the total kinetic energy contains some translational effects ("contamination").

4. It was shown in Ref. [21] that the only CM-dependent term arising in the analytic kinetic energy integral is the $R_{IJ}$ term defined in Eq. (32) of Ref. [21]:

$$
R_{IJ} = \frac{3}{2} \text{Tr} \left[ A_{IJ}^{(r)-1} A_{J}^{(r)} M A_{I}^{(r)} \right]
$$

$$
= \frac{3}{2} \text{Tr} \left[ (A_{IJ}^{(x)})^{-1} A_{J}^{(x)} U_x M U_T^{T} A_{I}^{(x)} \right]
$$

$$
= \frac{3}{2} \text{Tr} \left[ (A_{IJ}^{(x)})^{-1} A_{J}^{(x)} U^{(x)} A_{I}^{(x)} \right] + \frac{3}{4} c_A c_M
$$

Then, the translational contamination was eliminated by replacing $R_{IJ}$, with $R_{IJ} - 3c_A / (4m_{1\ldots N_p})$ in the expression of the kinetic energy matrix element (see Eqs. (33)–(37) of Ref. [21]).

At this point, we mention that the parameterization of the $A^{(r)}$ matrix expressed in Eq. (26) is the algebraic computation of the backward transformation from a specific TICC, namely the CMC coordinate set introduced in Eq. (7) to LFCC. This scheme therefore forces the $A^{(r)}$ matrix to be obtained from the block diagonal $A^{(x)}$ form through a specific mapping (a specific $U_x$ transformation matrix).

As to the generalization of this approach, we note that one can build more general schemes in which $A^{(x)}$ is mapped to the $A^{(r)}$ matrix by various transformations $U_a$, $a \in \{x, y, z, \ldots\}$ in order to enhance the flexibility of the basis functions, and thereby to gain direct access to
a broader region in the physical parameter space. The idea is related to the multi-coordinate or multi-channel optimization of Suzuki and Varga [25], also discussed by Mátys [7].

The present work generalizes the elimination approach of [21], summarized in Steps 1.–4., for the case of the multi-coordinate / multi-channel optimization. For this purpose we work out a fundamental relationships of the integral expressions corresponding to basis functions parameterized in different coordinate sets (defined by different $U_x$ and $U_y$ transformation matrices).

A. Fundamental relationships

First, we establish two mathematical relations that will be crucial in the extraction of $c_A$-dependent terms:

$$U_x\overline{A}_{IJ}^{-1}U_y^T = \begin{bmatrix} A_{IJ}^{-1} & 0 \\ 0 & \frac{1}{2c_A} \end{bmatrix}$$

and

$$U_yMU_x^T = \begin{bmatrix} \mu & 0 \\ 0 & \frac{c_M}{2} \end{bmatrix},$$

with $U_x$ and $U_y$ being the transformation matrices associated with two different TICC sets, Eqs. (2)–(4), for a pair of function $\phi_I$ and $\phi_J$, respectively. $A_{IJ}$ and $\mu$ are square matrices of dimension $N_p - 1$. $c_A$ is a free parameter and $c_M \equiv \frac{1}{2m_1 \ldots N_p}$ as will be determined below. $\bar{A}_{IJ}$ is an $(N_p \times N_p)$ matrix obtained as a sum of the $\bar{A}^{(r)}$ matrices of $\phi_I$ and $\phi_J$:

$$\bar{A}_{IJ} = \bar{A}^{(r)}_I + \bar{A}^{(r)}_J = U_x^T \bar{A}^{(x)}_I U_x + U_y^T \bar{A}^{(y)}_J U_y.$$

For later convenience, we write Eq. (27) in a different form:

$$U_x\overline{A}_{IJ}^{-1}U_y^T = \left(U_y^T \overline{A}_{IJ} U_x^{-1}\right)^{-1} = \begin{bmatrix} A_{IJ} & 0 \\ 0 & 2c_A \end{bmatrix}^{-1}$$

and

$$U_y^{-T} \bar{A}_{IJ} U_x^{-1} = U_y^{-T} \left(U_x^{-T} \bar{A}^{(x)}_I U_x + U_y^{-T} \bar{A}^{(y)}_J U_y\right) U_x^{-1} = U_y^{-T} U_x^{-T} \bar{A}^{(x)}_I + \bar{A}^{(y)}_J U_y U_x^{-1}.$$
So, we need to prove
\[
U_y U_x^{-1} = \begin{bmatrix} U & 0 \\ 0 & 1 \end{bmatrix},
\] (32)
to show the validity of Eq. (27). In simple terms, Eq. (32) means that the space of TICCs is closed: any linear combination of TICC coordinates is also a TICC coordinate (no contamination from the CMCC). It is easy to see qualitatively that this statement should be correct. The following equations provide the mathematical proof of it. During the derivation, we shall rely only on the properties of a \( U \) matrix, Eqs. (3) and (4), and general mathematical properties of determinants.

Let us consider \((U_y)_{ab} (U_x^{-1})_{bc}\) with \(U^{-1} = \frac{1}{\det(U)} \text{adj}(U)\) and \(\text{adj}(U) = C^T\) is the transpose of the cofactor matrix. Then,
\[
(U^{-1})_{iN_p} = \frac{C_{Npi}}{U_{Npi} C_{Np1} + \cdots + U_{NpN_p} C_{NpN_p}}.
\] (33)
Due to Eq. (3),
\[
C_{Npi} = \det \begin{pmatrix} U_{11} & \cdots & U_{1i-1} & U_{1i+1} & \cdots & (-U_{11} - U_{12} + \cdots - U_{1N_p}) \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ U_{Np-1 1} & \cdots & U_{Np-1 i-1} & U_{1i+1} & \cdots & (-U_{Np-1 1} - U_{Np-1 2} + \cdots - U_{Np-1 N_p}) \end{pmatrix},
\] (34)
and hence \(C_{Np1} = C_{Np2} = \cdots = C_{NpN_p}\). Moreover, we also have from Eq. (4) that
\[
(U^{-1})_{iN_p} = \frac{C_{Npi}}{(U_{Np1} + \cdots + U_{NpN_p}) C_{Np1}} = 1,
\] (35)
from which we obtain \(\det(U) = C_{Np1}\). From Eqs. (4) and (35), it follows that
\[
\sum_{b=0}^{N_p} (U_y)_{Npb} (U_x^{-1})_{bN_p} = 1
\] (36)
and
\[
\sum_{b=0}^{N_p} (U_y)_{ib} (U_x^{-1})_{bN_p} = 0 \text{ for } i \in \{0, N_p - 1\}.
\] (37)

To complete the proof, we need to show that
\[
\sum_{a=0}^{N_p} (U_y)_{Npa} (U^{-1})_{ai} = 0 \text{ for } i \in \{0, \ldots, N_p - 1\},
\] (38)
which is rewritten using Eq. (4) as:

\[
\frac{m_1}{m_{1...N_p} C_{N_p i}} C_{21} + \frac{m_2}{m_{1...N_p} C_{N_p i}} C_{22} + \ldots = \frac{1}{C_{N_p i}} \left( \frac{m_1}{m_{1...N_p} C_{21} + \frac{m_2}{m_{1...N_p} C_{22}} + \ldots} \right) = 0,
\]

(39)

where the term in the parenthesis is zero, because it is the determinant of a matrix with two identical rows. With this result, we have verified Eq. (27).

Next, we give the proof of Eq. (28) by investigating \(U_y M U_x^T\) element by element:

\[
(U_y M U_x^T)_{ij} = \sum_{k,l} (U_y)_{ik} M_{kl} (U_x^T)_{lj}
= \sum_k (U_y)_{ik} (U_x^T)_{kj} \frac{1}{2m_k}
= \sum_k (U_y)_{ik} (U_x)_{jk} \frac{1}{2m_k}.
\]

(40)

We can separate three cases

\[
\sum_k \frac{m_k}{m_{1...N_p}} \frac{1}{2m_k} = \sum_k \frac{m_k}{2m_{1...N_p}^2} = \frac{1}{2N_p} = \frac{c_M}{2}, \quad \text{for} \quad i = N_p \wedge j = N_p,
\]

\[
\sum_k \frac{1}{2m_k} (U_x)_{jk} = 0 \quad \text{for} \quad i = N_p \wedge j \in \{1, \ldots, N_p - 1\},
\]

\[
\sum_k (U_y)_{ik} \frac{1}{2m_k} = 0 \quad \text{for} \quad i \in \{1, \ldots, N_p - 1\} \wedge j = N_p,
\]

(41)

which completes the proof of Eq. (28).

Using the two fundamental relations, Eqs. (27) and (28), which we have just verified, we proceed to the identification of the CM-related terms in the integral expressions for the three types of ECG functions introduced in Section III C.

### B. Translationally invariant expressions for the pECG-type functions

The matrix element of the kinetic energy operator for pECG-type functions is

\[
T_{IJ} = \frac{\langle \phi_I | \nabla^T \nabla_r | \phi_J \rangle}{|\phi_I| |\phi_J|} = \frac{\langle \phi_I | \phi_J \rangle (\langle \phi_I | \phi_I \rangle \langle \phi_J | \phi_J \rangle)^{1/2}}{6 \text{ Tr} \left( \bar{A}^{-1} \bar{A}^{(r)} M \bar{A}^{(r)} \right)} = R
\]

(42)

The \(R\) term encompasses the total kinetic energy corresponding to the \(IJ\)-th matrix element and account for all particles. We investigate this term and isolate \(c_A\) contributions in order
to eliminate the center-of-mass kinetic energy contributions. The $c_A$-dependent terms cancel in the overlap integrals (see Appendix A), so, using Eqs. (27) and (28), we write

$$
R = \text{Tr} \left( A_{ij}^{-1} U_x \tilde{A}_{ij}^{(x)} U_y A_{ij}^{(y)} U_y \right) = \text{Tr} \left[ \begin{pmatrix} \tilde{A}_{ij}^{-1} & 0 \\ 0 & \frac{1}{2c_A} \end{pmatrix} \begin{pmatrix} \tilde{A}_{ij}^{(x)} & 0 \\ 0 & c_A \end{pmatrix} \begin{pmatrix} \mu & 0 \\ 0 & \frac{CM}{2} \end{pmatrix} \begin{pmatrix} \tilde{A}_{ij}^{(y)} & 0 \\ 0 & c_A \end{pmatrix} \right],
$$

(43)

Thereby, the contributions related to the overall translation are eliminated by subtracting the $c_A$ and $c_M$ dependent term(s):

$$
R^{(TI)} = R - \frac{1}{2} c_M c_A
$$

(44)

where the superscript TI refers to “translationally invariant” and $c_M$ has been introduced in Eq. (41).

C. Translationally invariant expressions for the FECG-type functions

The kinetic energy matrix element for FECG-type basis functions is [26]:

$$
T_{ij} = \frac{\langle \phi_i | \phi_j \rangle}{\left( \langle \phi_i | \phi_i \rangle \langle \phi_j | \phi_j \rangle \right)^{1/2}} \cdot \left[ 4 (s - s_I)^T A_i^{(r)} M A_j^{(r)} (s - s_J) + 6 \cdot \text{Tr} \left( M A_i^{(r)} A_{ij}^{-1} A_j^{(r)} \right) \right]_{\equiv Q} \text{Tr}(s - s_I)^T A_i^{(r)} A_{ij}^{-1} A_j^{(r)} M A_i^{(r)} A_{ij}^{-1} A_j^{(r)} (s - s_I),
$$

(45)

where $s = A_{ij}^{-1} \left( A_i^{(r)} s_i + A_j^{(r)} s_j \right)$ and every $s$ vector is expressed in the LFCC set (the superscripts $(r)$ have been omitted for clarity). For the $R$ term, we use the result obtained from the pECG functions, Eq. (44), so we need to consider the $Q$ term. First of all, we notice that:

$$
4 (s - s_I)^T A_i^{(r)} M A_j^{(r)} (s - s_J) = 4 (s_I - s_J)^T A_i^{(r)} A_{ij}^{-1} A_i^{(r)} M A_j^{(r)} A_{ij}^{-1} A_j^{(r)} (s_J - s_I),
$$

(46)

and thereby

$$
Q = 4 (s_I - s_J)^T A_i^{(r)} A_{ij}^{-1} A_i^{(r)} M A_j^{(r)} A_{ij}^{-1} A_j^{(r)} (s_J - s_I) \\
= 4 (s_I - s_J)^T \left[ U_x A_i^{(x)} U_x A_{ij}^{-1} U_y A_j^{(y)} U_y M U_x A_i^{(x)} U_x A_{ij}^{-1} U_y A_j^{(y)} U_y \otimes I_3 \right] (s_J - s_I) \\
= 4 (s_I - s_J)^T \left( \begin{pmatrix} \tilde{A}_i^{(x)} & 0 \\ 0 & c_A \end{pmatrix} \begin{pmatrix} \tilde{A}_{ij}^{-1} & 0 \\ 0 & \frac{1}{2c_A} \end{pmatrix} \begin{pmatrix} \tilde{A}_j^{(y)} & 0 \\ 0 & c_A \end{pmatrix} \begin{pmatrix} \mu & 0 \\ 0 & \frac{CM}{2} \end{pmatrix} \begin{pmatrix} \tilde{A}_i^{(x)} & 0 \\ 0 & c_A \end{pmatrix} \begin{pmatrix} \tilde{A}_{ij}^{-1} & 0 \\ 0 & \frac{1}{2c_A} \end{pmatrix} \begin{pmatrix} \tilde{A}_j^{(y)} & 0 \\ 0 & c_A \end{pmatrix} \otimes I_3 \right] (s_J - s_I),
$$

(47)
where Eqs. (27) and (28) are used in the third step. Finally, we identify the $c_A$-dependent terms in $Q$ as:

$$Q - Q_{TI}^T = \frac{1}{2} c_A c_M (s_I - s_J) \left[ (U^T_x)_i N (U_y)_N J \otimes I_3 \right] (s_J - s_I)$$

where $(U_q)_N J$ was defined in Eq. [4].

D. Translationally invariant expressions for the ECG-GVR-type functions

In this subsection, we consider the kinetic energy matrix element for ECG-GVR functions [7, 25]:

$$T_{IJ} = \left( \begin{align*}
&\left| 2A_I^{(r)} \right|^2 \left| 2A_J^{(r)} \right|^2 \\
&\frac{1}{A_I^{(r)} + A_J^{(r)}}
\end{align*} \right)^{\frac{3}{2}} \left( \begin{array}{cc}
&K_I \\
&K_J
\end{array} \right) \left( \begin{array}{cc}
&\frac{P_{u_I, u_J}}{q_{u_I}} \\
&\frac{P_{u_J, u_J}}{q_{u_J}}
\end{array} \right)^L \times \min(K_I, K_J) \sum_{m=0}^{\min(K_I, K_J)} \left( \frac{P_{u_I, u_J}}{P_{u_J, u_J} P_{u_I, u_J}} \right)^m \left[ \frac{3}{2} R + (K_I - m) \frac{P_{u_I, u_J}}{P_{u_I, u_I}} \right] H_{NK_I K_J M},
$$

where

$$p_{u_Q, u_Z} = u_Q^T \bar{A}_{IJ}^{-1} u_Z,$$

$$P_{u_I, u_J} = -u_I^T \bar{A}_{IJ}^{-1} \bar{A}_J^{(r)} M \bar{A}_J^{(r)} \bar{A}_{IJ}^{-1} u_I,$$

$$P_{u_J, u_J} = -u_J^T \bar{A}_{IJ}^{-1} \bar{A}_I^{(r)} M \bar{A}_I^{(r)} \bar{A}_{IJ}^{-1} u_J,$$

$$P_{u_I, u_J} = u_I^T \bar{A}_{IJ}^{-1} \bar{A}_J^{(r)} M \bar{A}_J^{(r)} \bar{A}_{IJ}^{-1} u_J,$$

$$q_{u_Z} = \frac{1}{2} u_Z^T \bar{A}_{IJ}^{-1} u_Z,$$

$$R = \text{Tr} \left[ \bar{A}_{IJ}^{-1} \bar{A}_J^{(r)} M \bar{A}_J^{(r)} \right].$$

with $Q, Z \in \{I, J\}$ and $H_{NK_I K_J M}$ is a set of precomputed values defined in Ref. [7]. Among these, only $R$ and $P$ terms arise from the application of the kinetic operator on the bra and the ket ECG-GVR functions.

In Ref. [21], the constraint $c_U = 0$ was introduced in order to facilitate the elimination of CM contributions from the terms in Eqs. (50)-(55). Here we provide formulas for the elimination of CM kinetic energy that consider a non trivial value for $c_U$. 

15
We calculate the corrections to the only terms generated by the kinetic energy integral on the generating functions (see Eq. (S34) in Ref. [7]), that is, \( R, P_{u_j,u_i}, P_{u_i,u_j} \) and \( P_{u_i,u_j} \). Using Eqs. (23)–(24) and then Eqs. (27)–(28) we write:

\[
P_{u_j,u_i} = u^{(x)}_I U_x A^{-1}_{I,J} U^T_y A^{(y)}_J U_y M U^T_x A^{(x)}_I U_x A^{-1}_{I,J} U^T_y u^{(y)}_J
\]

\[
= \left( \begin{array}{c} u'_I \end{array} \right) \left( \begin{array}{cc} A^{-1}_{I,J} & 0 \\ 0 & \frac{1}{2c_A} \end{array} \right) \left( \begin{array}{cc} A^{(y)}_J \\ 0 \end{array} \right) \left( \begin{array}{cc} \mu \\ 0 \end{array} \right)
\]

\[
\quad \quad \quad \cdot \left( \begin{array}{c} A^{(x)}_I \\ 0 \end{array} \right) \left( \begin{array}{cc} A^{-1}_{I,J} & 0 \\ 0 & \frac{1}{2c_A} \end{array} \right) \left( \begin{array}{c} u'_J \end{array} \right)
\]

and analogous expressions are obtained for \( P_{u_i,u_j} \) and \( P_{u_i,u_j} \). As a result, the translationally invariant (TI) expressions are

\[
P^{\text{TI}}_{u_j,u_i} = P_{u_j,u_i} - \frac{1}{4} c_{U_j} c_{M} c_{U_i},
\]

\[
P^{\text{TI}}_{u_i,u_j} = P_{u_i,u_j} + \frac{1}{4} c_{U_j} c_{M} c_{U_i},
\]

\[
P^{\text{TI}}_{u_i,u_j} = P_{u_i,u_j} + \frac{1}{4} c_{U_j} c_{M} c_{U_j}.
\]

Furthermore, \( R \) in Eq. (49) is replaced with \( R^{\text{TI}} \) given in Eq. (44), which completes the list of expressions which will be used to eliminate the effect of the overall translation in LFCC calculations carried out with the ECG-GVR-type functions.

### E. Multi-channel optimization

The exact wave function is estimated as a linear combination of (anti)symmetrized products of spin and spatial functions in a variational procedure. The linear combination coefficients are determined by solving the generalized eigenvalue problem. In what follows, we shall discuss in detail how we parameterize the spatial basis functions. The spatial functions are generated one after the other and (their parameters) are optimized variationally using the competitive selection procedure [25]. In order to obtain very accurate energy levels, we repeatedly fine-tune the parameters of the selected basis functions using Powell’s method [27]. The convergence of the computed states is ensured by the variational principle. As an additional check, we also calculate the virial ratio.

The efficiency of the optimization procedure can be enhanced by tuning the basis function parameters expressed in different translationally invariant coordinate sets. Qualitatively
speaking, different TICC sets describe efficiently different “groupings” of the particles (pairs and triples of particles, etc.). The basis functions which describe the interaction of these pairs or groups of particles can be directly expressed in that particular TICC representation. So, the calculations (Hamiltonian representation, matrix elements, etc.) are performed in laboratory-fixed Cartesian coordinates, but the optimization of the basis function parameters is carried out by (automatically) cycling through several TICC representations. In principle, any (of the infinitely many possible) TICC set is allowed for which the $U$ transformation matrix satisfies Eqs. (12)–(20). This multi-coordinate optimization procedure is known as multi-channel optimization in the literature [25] where channel refers to a particular coordinate selection.

In the competitive selection procedure, to generate a new basis function, the basis function parameters are sampled from a normal probability distribution. The mean and variance values, which determine the distribution used, are determined during the calculations by analyzing the already selected basis-set parameters.

F. Numerical results

In this section, we present numerical results of calculations carried out in laboratory-fixed Cartesian coordinates. For the optimization of the basis function parameters we used several coordinate sets ("channels") in order to find more efficiently the optimal parameter set describing the correlations (and in general, interactions) between pairs and groups of particles.

Tables I and II present numerical results of this procedure obtained for the ground state of the para-H$_2^+$ ($N = 0$) and para-H$_2$ ($N = 0$) molecular species using the FECG and the ECG-GVR-type functions. In the tables we show both the full LFCC energies, which include translational effects as well as the "corrected", translation-free ("translationally invariant", TI) energies, which are indeed smaller and which reproduce the values obtained in some translationally invariant formulation of the Hamiltonian in the literature.

The translation-free energies are obtained by using the CM-elimination formulae in Eqs. (44), (48) and (57) derived in the earlier sections. In the case of FECG's functions, we also calculate translationally invariant total angular momentum squared expectation values $\langle \hat{N}^2 \rangle_{TI}$ to observe the contamination from excited rotational states. The systematic
TABLE I: Pre-Born–Oppenheimer ground-state energies, in Hartree atomic units, of the para spin state of H$_2^+$ = \{p$^+$, p$^+$, e$^-$\} as well the para spin state of H$_2$ = \{p$^+$, p$^+$, e$^-$, e$^-$\}.

The results were obtained with the FECG-type functions, which are not angular momentum eigenfunctions, and hence the expectation value of the translationally invariant total orbital angular momentum squared operator, $\hat{N}^2_{TI}$, is also given.

| $\langle \hat{H} \rangle_{\text{LFCC}}$ | $\eta$ | $a\langle \hat{H} \rangle_{\text{TI}}$ | $b\langle \hat{N}^2_{\text{TI}} \rangle$ | $c\eta_{\text{TI}}$ |
|--------------------------------|---------|--------------------------------|-----------------|-----------------|
| $p$–H$_2^+$ (ground state) $N_b = 400$ | -0.596231 $10^{-2}$ | -0.597024 | 11.26 | $10^{-4}$ |
|                                      | -0.596988 $10^{-2}$ | -0.597012 | 9.11 | $10^{-4}$ |
|                                      | -0.593754 $10^{-2}$ | -0.597032 | 18.30 | $10^{-4}$ |
|                                      | -0.596845 $10^{-2}$ | -0.597006 | 10.81 | $10^{-4}$ |
|                                      | -0.595096 $10^{-2}$ | -0.597044 | 11.48 | $10^{-4}$ |
| $p$–H$_2$ (ground state) $N_b = 600$ | -1.162147 $10^{-2}$ | -1.162686 | 10.59 | $10^{-4}$ |
|                                      | -1.162263 $10^{-3}$ | -1.162696 | 10.22 | $10^{-4}$ |
|                                      | -1.161655 $10^{-2}$ | -1.162721 | 14.47 | $10^{-4}$ |
|                                      | -1.161490 $10^{-2}$ | -1.162669 | 15.01 | $10^{-4}$ |
|                                      | -1.160502 $10^{-1}$ | -1.162690 | 19.66 | $10^{-4}$ |

$^a$ translationally invariant energy expectation value obtained by eliminating CM contributions from the total kinetic energy;

$^b$ translationally invariant total angular momentum squared expectation value $\langle \hat{N}^2_{\text{TI}} \rangle$

$^c$ translationally invariant virial coefficient, $\eta_{\text{TI}} = \left| 1 + \langle \Psi | \hat{V} | \Psi \rangle / 2 \langle \Psi | \hat{T} | \Psi \rangle_{\text{TI}} \right|$

study of these contributions and the analytical expressions for this expectation value will be the presented in a later study.

In the multi-channel optimization approach, we have included every possible set of Jacobi coordinates, “heavy-particle”-centered (HCP) coordinates as well as the center-of-mass-centered (CMC) coordinates are included. (The optimized basis function parameters are deposited in the Supplementary Material [32].) The virial coefficient, $\eta = \left| 1 + \langle \Psi | \hat{V} | \Psi \rangle / 2 \langle \Psi | \hat{T} | \Psi \rangle_{\text{TI}} \right|$, vanishes for the exact solution (according to the virial theorem [23]),
TABLE II: Pre-Born–Oppenheimer ground-state energies, in Hartree atomic units, of the para spin state of H$_2^+$ = {p$,^+$, p$^+$, e$^-$} as well the para spin state of H$_2$ = {p$,^+$, p$^+$, e$^-$, e$^-$}.

The results were obtained with ECG–GVR-type functions with $K_{\text{max}} = 20$.

|                  | $\langle \hat{H} \rangle_{\text{LFCC}}$ | $\eta$ | $^{a} \langle \hat{H} \rangle_{\text{TI}}$ | $^{b} \eta_{\text{TI}}$ | $^{c} \delta E/\mu E_h$ |
|------------------|------------------------------------------|--------|-------------------------------------------|--------------------------|--------------------------|
| $p$–H$_2^+$ ($N = 0, M_N = 0$) $N_b = 180$ |                                           |        |                                           |                          |                          |
| SC$^d$           | -0.59(67)                                | $10^{-3}$ | -0.597138979                              | $10^{-8}$                | -0.084                   |
|                  | -0.59(67)                                | $10^{-3}$ | -0.597139061                              | $10^{-8}$                | -0.002                   |
|                  | -0.59(65)                                | $10^{-3}$ | -0.597139059                              | $10^{-8}$                | -0.004                   |
|                  | -0.59(65)                                | $10^{-2}$ | -0.597139057                              | $10^{-8}$                | -0.006                   |
|                  | -0.59(61)                                | $10^{-2}$ | -0.597139059                              | $10^{-8}$                | -0.004                   |
|                  | -0.59(55)                                | $10^{-2}$ | -0.597139058                              | $10^{-8}$                | -0.006                   |
|                  |                                           |        |                                           |                          |                          |
| $p$–H$_2$ ($N = 0, M_N = 0$) $N_b = 500$ |                                           |        |                                           |                          |                          |
| SC$^d$           | -1.16(35)                                | $10^{-3}$ | -1.164024880                              | $10^{-7}$                | -0.146                   |
|                  | -1.16(38)                                | $10^{-3}$ | -1.164025023                              | $10^{-8}$                | -0.007                   |
|                  | -1.16(36)                                | $10^{-2}$ | -1.164025026                              | $10^{-8}$                | -0.004                   |
|                  | -1.16(35)                                | $10^{-2}$ | -1.164025026                              | $10^{-8}$                | -0.004                   |
|                  | -1.16(30)                                | $10^{-2}$ | -1.164025028                              | $10^{-8}$                | -0.002                   |
|                  | -1.16(31)                                | $10^{-1}$ | -1.164025024                              | $10^{-8}$                | -0.006                   |

$^a$ translationally invariant energy expectation values obtained by eliminating CM contributions from the total kinetic energy;

$^b$ translationally invariant virial $\eta_{\text{TI}} = |1 + \langle \Psi |\hat{V}|\Psi \rangle /2\langle \Psi |\hat{T}|\Psi \rangle_{\text{TI}}|$

$^c$ $\delta E = E($Ref.$) - \langle \hat{H} \rangle_{\text{TI}}$;

$E_{p–H_2^+}/E_h = -0.597139063$ from Ref. [28, 29], $E_{p–H_2}/E_h = -1.164025030$ from Ref. [30, 31]

$^d$ single-channel calculation corresponding to a single Jacobi-coordinate set.

so it is used as an additional indicator for the overall quality of the variationally optimized wave function.

The FECG-type functions are not eigenfunctions of the total angular momentum operators, $\hat{N}^2$ and $\hat{N}_z$, and the parity. These symmetry properties of the exact solution are
restored numerically by the variational optimization procedure. In the calculations, the obtained total angular momentum expectation value, $\langle N^2 \rangle_{\text{TI}}$ (see Table I) is about 10, which corresponds to an effective angular momentum value of about 2.7 to be compared with the $N = 0$ value of the absolute ground state. We include these results in the present article in order to explore the numerical behavior of FECG-type functions. Future work might consider numerical techniques, which project the FECG functions onto irreps of the SO(3) rotation group.

In order to reproduce literature data computed in some translationally invariant representation of the coordinates and the Hamiltonian, we also used the ECG-GVR-type functions (see Table II), which are eigenfunctions of the total angular momentum operators and also the space inversion. Our results reproduce the literature data within a few nano Hartree accuracy. The significantly lower number of the basis functions (500 with respect to 2000) in comparison to earlier work using a single TICC set in the optimization [7, 16, 21], indicate the efficiency of the multi-channel optimization procedure developed in the present work. In spite of the multiple coordinate sets used for the parameter optimization, we solve the Schrödinger equation (and calculate integrals) in simple laboratory-fixed Cartesian coordinates. Translation-free energies are obtained after the elimination of center-of-mass effects (compare the $\hat{H}_{\text{LFCC}}$ and $\hat{H}_{\text{TI}}$ columns of Table II).

V. SUMMARY AND CONCLUSIONS

The article presents further progress about the solution of the many-particle Schrödinger equation in laboratory-fixed Cartesian coordinates (LFCCs). We extend our earlier work using explicitly correlated Gaussian (ECG) functions [21] to be applicable with a more efficient basis-function parameter optimization procedure, called multi-channel optimization. Multi-channel optimization relies on the optimization of the interaction of several possible pairs and groups of particles (“channels”) of the many-particle system by repeatedly changing the pairing or grouping of the particles. This idea is realized in our work by transforming the basis function parameterization back and forth during the optimization procedure between the different particle groups or channels, which, after all, are represented by some coordinate set, while we solve the Schrödinger equation (Hamiltonian, matrix elements, etc.) in simple LFCCs and obtain translationally invariant (TI) properties.
In order to implement these general ideas in an algorithm and computer code, we study the form of the basis functions and the mathematical expressions of the Hamiltonian matrix elements upon the transformation of the coordinates between LFCCs and various translationally invariant sets of Cartesian coordinates and the center-of-mass coordinates (TICCs and CMCCs). We also work out the formal equations which prove that the various (infinitely many) possible sets of TICCs form a closed set and can be combined arbitrarily without introducing any contamination from the center of mass coordinates (see Section IV A). Using these results, we identify the center-of-mass (CM) terms in the kinetic-energy integral expressions for three particular types of ECG functions, which is necessary for the multi-channel implementation. Translationally invariant energies are obtained from an LFCC Hamiltonian by eliminating these CM terms during the course of the integral evaluation procedure, performed in LFCCs.

The applicability and efficiency of this new algorithm and computer code is demonstrated for the ground state of the three-particle $H_2^+ = \{p^+, p^+, e^-\}$ as well as of the four-particle $H_2 = \{p^+, p^+, e^-, e^-\}$ molecular systems. We solve the many-particle Schrödinger equation in laboratory-fixed Cartesian coordinates and eliminate the translational contamination during the integral evaluation, while we optimize the basis-function parameters using multiple channels (coordinates) including all possible Jacobi coordinates, all possible heavy-particle-centered coordinate arrangements, as well as the center-of-mass-centered coordinate set.

Our present LFCC formalism allows an increased flexibility of the basis functions and a better energy convergence. It is an alternative to the traditional approaches using some set of TICCs with the Cartesian coordinates of the center of mass explicitly separated out from the Hamiltonian.

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Appendix A: Center-of-mass contributions to the overlap integral for pECG functions

The normalized overlap matrix element $I J$-th for pECG functions is

$$\frac{\langle \phi_I | \phi_J \rangle}{\langle \langle \phi_I | \phi_I \rangle \langle \phi_J | \phi_J \rangle} = \left( \frac{\left| 2 \bar{A}^{(r)}_I \right|^2 \left| 2 \bar{A}^{(r)}_J \right|^2}{\left| A^{(r)}_I + \bar{A}^{(r)}_J \right|^2} \right)^{\frac{1}{2}}. \quad (A1)$$

Similarly to Sec. (IV) we identify $c_A$-related terms, which are associated to the center-of-mass coordinate. Firstly, we can rewrite the expressions as

$$\left( \left| 2U^T x A^{(x)}_I U_x \right| \cdot \left| 2U^T y A^{(y)}_J U_y \right| \cdot \left| A^{(r)}_I \right| \cdot \left| \bar{A}^{(r)}_J \right| \right)^{\frac{1}{2}}, \quad (A2)$$

and employ the properties of determinants, $|A \cdot B| = |A| \cdot |B| = |B \cdot A|$ and $|A^{-1}| = |A|^{-1}$, to arrive at

$$\left| 4 \cdot U^T x A^{(r)}_I U_x \cdot A^{(x)}_I \cdot U^T y A^{(r)}_J U_y \cdot \bar{A}^{(y)}_J \right|. \quad (A3)$$

If different $c_{A_I}$ and $c_{A_J}$ values were allowed for the $I$th and $J$th basis functions, we obtained

$$\left| 4 \cdot \begin{pmatrix} A^{-1}_{I,J} & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} A^{(x)}_I & 0 \\ 0 & c_{A_I} \end{pmatrix} \begin{pmatrix} A^{-1}_{I,J} & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} A^{(y)}_J & 0 \\ 0 & c_{A_J} \end{pmatrix} \right|. \quad (A4)$$

Contributions from the $c_A$ factors cancel only if $c_{A_I} = c_{A_J}$.

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Supplementary Material Document No. XXX contains the optimized basis function parameters for the ground state of the para-H$_2^+$ and for the para-H$_2$ molecular systems.