Analytically projected rotationally symmetric explicitly correlated Gaussians with one-axis shifted centers

Andrea Muolo and Markus Reiher

ETH Zürich, Laboratory of Physical Chemistry, Vladimir-Prelog-Weg 2, 8093 Zürich, Switzerland

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Abstract

A new explicitly correlated functional form for expanding the wave function of an $N$-particle system with arbitrary angular momentum and parity is presented. We develop the projection-based approach, numerically exploited in our previous work [J. Chem. Phys. 149, 184105 (2018)], to explicitly correlated Gaussians with one-axis shifted centers and derive the matrix elements for the Hamiltonian and the angular momentum operators by analytically solving the integral projection operator. Variational few-body calculations without assuming the Born-Oppenheimer approximation are presented for several rotationally excited states of three- and four-particle systems. We show how the new formalism can be used as a unified framework for high-accuracy calculations of properties of small atoms and molecules.
I. INTRODUCTION

Highly accurate bound states of the Schrödinger equation for small atoms and molecules can be constructed by expanding the wave function in terms of basis functions depending explicitly on inter-particle distances \([1–13]\). Non-separable functions with respect to the particle coordinates are tailored to describe particle-particle correlations, especially to accurately reproduce the exact wave function for infinitesimally short distances and in the long range limit. Furthermore, they allow for a unified treatment of different kinds of particles, \(e.g.\) of electrons and nuclei. Within this framework, two- and three-electron atoms can be very accurately calculated employing Hylleraas-type functions \([7, 14–18]\) that explicitly include powers of the inter-electronic distances \(r_{ij} = |r_i - r_j|\). However, the difficulties of the analytical calculation of their matrix elements prevent application of this approach to larger systems \([19, 20]\). Generality with respect to the particle number and accessible analytical Hamiltonian matrix elements are achievable through powers of the quadratic form of the inter-particle distances that define explicitly correlated Gaussians (ECGs) \([1, 2]\). Plain Gaussian functions are also manifestly spherically symmetric, \(i.e.\) invariant under rotation. Although these two properties made ECG-like functions very popular in high accuracy calculations \([3, 4, 6, 8, 9, 21]\), the spherical symmetry limits the applicability of plain ECGs to ground rotational states only. Different approaches \([22, 23]\) have been developed to extend ECGs to nonspherical problems, \(i.e.\) for calculating states with non-zero total spatial angular momentum quantum number \(N\).

In general, the ECGs are being multiplied with a nonspherical function \(\theta_{NM,N}(r)\) of the collective position vectors \(r\) that for one particle in a central potential would just reduce to a solid spherical harmonic \(Y(r_1)\). The generalization to the \(N_p\)-particle case is a vector-coupled product of the solid spherical harmonics of the relative coordinates,

\[
\theta_{NM,N}(r) = \sum_{\kappa=\{m_1,m_2,...,m_{N_p}\}}^{N_p} C_{\kappa} \prod_{i=1}^{N_p} Y_{l_i m_i}(r_i), \tag{1}
\]

where \(C_{\kappa}\) is a product of Clebsch–Gordan coefficients,

\[
C_{\kappa} = \langle l_1 m_1 l_2 m_2 | L_{12} m_1 + m_2 \rangle \langle L_{12} m_1 + m_2 l_3 m_3 | L_{123} m_1 + m_2 + m_3 \rangle \cdots \langle L_{12...N_{p}−1} m_1 + m_2 + \ldots + m_{N_p−1} l_{N_{p} m_{N_{p}}} | N M_N \rangle, \tag{2}
\]

that couples the orbital angular momenta sequentially to the specified total quantum num-
bers \((N, M_N)\). Since the angular momentum of the relative motion is not a conserved quantity, it is important for an accurate description to include several sets of orbital angular momenta \((l_1, l_2, \ldots, l_N; L_{12}, L_{123}, \ldots)\) weighted by \(C_\kappa\). Eq. (1) is a partial-wave expansion whose direct implementation is cumbersome since the matrix elements for this choice of \(\theta_{NM_N}(r)\) will become very complicated. Moreover the algebraic complexity of the integral matrix elements is not invariant with respect to the number of particles, and hence, analytical expressions must be derived for each different system.

One viable alternative to the full partial wave decomposition is to consider only limited coupling schemes “specializing” the basis functions for a given \(N\) while the relative matrix elements are explicitly derived. For example, Refs. [24–28] focused on ECG functions specifically tailored for \(N = 1\) states considering the sets of orbital angular momenta \((l_1 = 0, \ldots, l_i = 1, \ldots, l_{N_p} = 0)\). Ref. [29–32] tackled \(N = 2\) states analogously with lowest-order angular momentum couplings.

Alternatively, representations of \(\theta_{NM_N}(r)\) including the orientation of a global vector \(v\) formed as a linear combination of all particle coordinates \(\{r_i\}\), have been successfully employed in high-accuracy calculations of properties of small atoms and molecules [10, 33]. This approach is based on an equivalence condition between the global vector representation of \(\theta_{NM_N}(r)\) and the partial-wave expansion for a given orientation of the global vector. Under the assumption of a smooth energy landscape in parameter space, the global vector orientation can be recovered variationally through the minimization of the energy with respect to its real-valued parameters. Although this approach is appealing because it yields analytical matrix elements for quantum mechanical operators that are form invariant with respect to the angular momentum quantum numbers \(N\) and \(M_N\), and the number of particles \(N_p\), the variational optimization of the global vector parameters is difficult and not every \(\theta_{NM_N}(r)\) can be represented. These alternative formulations are strictly derived from the partial wave expansion as a result of having truncated or variationally approximated Eq. (1).

In this work, we extend our numerical projection scheme onto irreducible representations of the rotational-inversion \(O(3)\) group presented in our previous work [34], focusing on a special case where the integral projector can now be solved analytically. In Ref. [34], we considered explicitly correlated Gaussians with centers shifted by a vector in the three-dimensional Euclidean space, \(s \in \mathbb{R}^3\). Numerically exact eigenfunctions of the squared total spatial angular momentum operator \(\hat{N}^2\) and the parity operator \(\hat{p}\) were then constructed.
with explicit projection onto the corresponding eigenspace. We relied on numerical quadrature schemes for the calculation of integral matrix elements which introduced noticeable computational cost in the variational iterative steps. In practice, numerical projection precludes large basis sets from being optimized variationally and limits the applicability of the developed formalism. Here, we consider solving exactly the projection operator for a subset of floating ECG functions having shifted centers along only one axis. We devise analytical integral matrix elements for projected functions for the overlap, kinetic, Coulomb, and angular momentum operators. We illustrate the validity of this novel functional form by studying the first three rotational states of the dihydrogen molecular ion, \( \text{H}_2^+ = \{p^+, p^+, e^-\} \) treated explicitly as a three particle system.

II. THEORY

We consider a non-relativistic Coulombic Hamiltonian for \( N_p \) particles

\[
\hat{H}_{\text{lab}} = -\nabla_r^T M \nabla_r + \sum_{i=1}^{N_p} \sum_{j>i}^{N_p} \frac{q_i q_j}{|r_i - r_j|}, \tag{3}
\]

with the position vector \( r_i \) of the \( i \)th particle in the laboratory fixed Cartesian coordinates (LFCC), its mass \( m_i \) and its charge \( q_i \). \( \nabla_r \) is the gradient with respect to \( r_i \) and \( M \) is a \( N_p \times N_p \) matrix with elements \( M_{ij} = \delta_{ij}/2m_i \).

As we are interested in bound states, the motion of the center of mass can be discarded. This is usually realized by a linear transformation of the coordinates

\[
U_x r = (x_1, x_2, \ldots, x_{N_p-1}, x_{\text{CM}})^T \tag{4}
\]

in which the \( x_{\text{CM}} = \sum_{i=1}^{N_p} m_i r_i / (\sum_{i=1}^{N_p} m_i) \) are the center-of-mass Cartesian coordinates (CMCC) and \( x \equiv (x_1, \ldots, x_{N_p-1}) \) denotes the translationally invariant Cartesian coordinates (TICC) corresponding to the internal coordinates of the system generated through the relative transformation matrix \( U_x \). A transformation of the Hamiltonian in Eq. (3) separates the kinetic energy term for the center of mass from the internal Hamiltonian [23, 35]:

\[
\hat{H}_{\text{int}} = -\nabla_x^T \mu \nabla_x + \sum_{i=1}^{N_p-1} \sum_{j>i}^{N_p-1} \frac{q_i q_j}{|(f_{ij} \times \mathbf{\hat{e}}_3)_x|}, \tag{5}
\]

where

\[
\mu = U_x^{-T} M U_x, \tag{6}
\]
This separation of the center-of-mass coordinate requires transforming both the Hamiltonian and the state function and has been exploited in practice [9, 10].

By contrast, here we solely transform the basis functions in a given TICC set without transforming quantum mechanical operators following the method described in our previous work [36, 37]. In this approach, the matrix-element calculations are carried out naturally in the LFCC set and the center-of-mass contamination is rigorously subtracted from the expectation values. While handling state functions in a TICC set is very appealing because of the restriction of the parameter space to only \(N_p - 1\) internal coordinates, we avoid the difficulties arising from matrix elements for transformed operators and instead retain the algebraic simpler and intuitive LFCC set for the integral evaluation. We employ the heavy-particle centered, the center-of-mass centered, and Jacobian Cartesian coordinate sets, allowing the basis functions to cycle through these TICC representations in order to describe efficiently different "groupings" of particles (e.g., pairs and triples of particles).

### III. BASIS FUNCTIONS

Given the total spin quantum number and its projection on the z-axis \(S\) and \(M_s\), respectively, the wave function representing is expanded as a linear combination of (anti-)symmetrized floating explicitly correlated Gaussians (FECGs)

\[
\Psi(\mathbf{r}) = \sum_{I=1}^{N_b} c_I \chi^{S,M_S}_I \hat{Y} \phi^{\text{FECG}}_I(\mathbf{r}; \{\omega_I\}),
\]

where \(c_I\) are the expansion coefficients, \(\chi^{S,M_S}_I\) are spin functions, and \(\hat{Y}\) is the Young operator that accounts for the appropriate permutation symmetry of sets of identical particles as described by Kinghorn [38]. Floating explicitly-correlated Gaussians (FECG) have the following general form

\[
\phi^{[\text{FECG}]}_I = \exp \left[ - (\mathbf{r} - \mathbf{s}_I)^T (A_I \otimes 1_3) (\mathbf{r} - \mathbf{s}_I) \right].
\]

Here, \(A_I\) is a \(N_p \times N_p\) symmetric matrix of \(\frac{1}{2}N_p(N_p + 1)\) variational parameter with the subscript \(I\) indicating that they are unique for each basis function. It is \(\mathbf{r}(A_I \otimes 1_3)\mathbf{r} >\)
∀ \boldsymbol{r} \in \mathbb{R}^{3N_p}, that is \( A_I \) must be positive definite, to ensure square integrability of the \( \phi_I^{[\text{FECG}]} \) basis function. A necessary and sufficient condition for a symmetric real matrix to be positive definite is that all eigenvalues are positive. Here \( \boldsymbol{r} - \boldsymbol{s}_I \) stands for a set of vectors \( \{ \boldsymbol{r}_1 - \boldsymbol{s}_{I1}, \ldots, \boldsymbol{r}_{N_p} - \boldsymbol{s}_{IN_p} \} \) that correspond to shifted particle coordinates with the \( 3N_p \)-dimensional vector \( \boldsymbol{s}_I \) composed of parameters to be optimized in a variational procedure.

In the following sections we explicitly work out the integral matrix elements in the simple LFCC frame.

IV. PROJECTION TECHNIQUE

The FECGs in Eq. (9) define Gaussians with shifted centers to allow for suitable deformations of the ansatz for the all-particle wave function that are predominantly needed for polyatomic systems [23, 37]. A general FECG function is, however, neither an eigenfunction of the squared total angular momentum operator \( \hat{\boldsymbol{N}}^2 \), nor an eigenfunction of the space inversion operator \( \hat{\hat{p}} \). As the rotation-inversion symmetry must be restored variationally in the limit of a complete basis set, these basis functions gives rise to poor energy convergence.

To alleviate this problem, we recently proposed an integral projection operator, \( \hat{P}_{MN}^{[N,p]} \) [34], to ensure the correct spatial rotation-inversion symmetry corresponding to \( N \) and \( M_N \), the total spatial angular momentum quantum numbers, and the parity quantum number \( p \):

\[
\hat{P}_{MN}^{[N,p]} = \hat{P}_{MN,MN}^{[N]} \hat{P}_{CI}^{[p]},
\]

with

\[
\hat{P}_{MN,MN}^{[N]} = \int d\Omega \frac{d\Omega}{4\pi^3} D_{MN,MN}^{[N]} (\Omega)^* \hat{R}(\Omega),
\]

and

\[
\hat{P}_{CI}^{[p]} = \hat{\mathcal{E}} + \hat{p} \cdot \hat{\mathcal{I}},
\]

where \( \hat{\mathcal{E}} \) is the identity operator, \( \hat{\mathcal{I}} \) is the spatial inversion operator, and \( D_{MN,MN}^{N} \) the diagonal element of the \( N \)-th Wigner \( D \)-matrix with \( \hat{R}(\Omega) \) being the quantum mechanical rotation operator over the Euler angles \( \Omega \equiv \{ \alpha, \beta, \gamma \} \) [39],

\[
\hat{R}(\alpha, \beta, \gamma) = \exp(-i\alpha N_z) \exp(-i\beta N_y) \exp(-i\gamma N_z).
\]
The effect of the projector operator in Eq. (10) on a state $|N M_N\rangle$ is

$$\hat{P}_{M_1M_2}^{[N_1]} |N_2M_2\rangle = |N_1M_1\rangle \delta_{N_1N_2} \delta_{M_1M_2} ,$$

(14)

with $|NM_N\rangle$ being angular momentum eigenstates. Note that our original implementation [34] of the projection scheme was purely numerical, which we overcome in this work for the special case of projection on one spatial axis, for which analytical expression can be derived.

The form of the rotation operators in Eq. (13) is not a convenient operational definition because they require an explicit expression of the angular momentum components $N_i$ that is not entirely straightforward in our all-particle explicitly-correlated formulation. Nonetheless, exactly the same symmetry operation will be realized if we rotate the physical system itself or if we rotate the coordinate axis in the opposite direction,

$$\hat{R}(\Omega)\phi_{I}^{\text{FECC}}(r; A_I, s_I) = \phi_{I}^{\text{FECC}}(U(\Omega)^{-1} r; A_I, s_I)$$

$$= \exp\left[ -(U(\Omega)^{-1} r - s_I)^T (\hat{A}_I^{(r)} \otimes 1_3) (U(\Omega)^{-1} r - s_I) \right]$$

$$= \exp\left[ -(r - U(\Omega)s_I)^T (\hat{A}_I^{(r)} \otimes \bar{U}(\Omega)^{-1}) (r - U(\Omega)s_I) \right]$$

$$= \phi_{I}^{\text{FECC}}(r; A_I, U(\Omega)s_I) ,$$

(15)

where $U(\Omega) = 1_3 \otimes \bar{U}(\Omega)$ represents the coordinate transformation generalized to a system of $N_p$ particles with

$$\bar{U}(\Omega) = \begin{pmatrix} \cos \alpha \cos \beta \cos \gamma - \sin \alpha \sin \gamma & - \cos \alpha \cos \beta \sin \gamma - \cos \alpha \sin \beta \\ \cos \beta \cos \gamma \sin \alpha + \cos \alpha \sin \gamma & \cos \alpha \cos \beta - \cos \beta \sin \alpha \sin \gamma - \sin \alpha \sin \beta \\ \cos \gamma \sin \beta & \sin \beta \sin \gamma & \cos \beta \end{pmatrix} ,$$

(16)

The properties of the rotation operator are summarized in four commutation relations:

$$\left[ \hat{R}(\Omega), \hat{H} \right] = 0 ,$$

(17)

$$\left[ \hat{R}(\Omega), \hat{N}_2 \right] = 0 ,$$

(18)

$$\left[ \hat{R}(\Omega), \hat{N}_z \right] \neq 0 ,$$

(19)

$$\left[ \hat{R}(\Omega), \hat{P} \right] = 0 .$$

(20)

Furthermore, the $\hat{P}_{M_NM_N}^{[N]}$ projection operator is idempotent and Hermitian:

$$(\hat{P}_{M_NM_N}^{[N]})^2 = \hat{P}_{M_NM_N}^{[N]}$$

(21)

$$(\hat{P}_{M_NM_N}^{[N]})^\dagger = \hat{P}_{M_NM_N}^{[N]} .$$

(22)
Properties in Eqs. (17)-(22) will be employed in the remainder of this work for the calculation of quantum mechanical expectation values.

V. MATRIX ELEMENTS

In this section, we present analytical projected FECGs matrix elements for important operators in the special case of unidimensional shift vectors, that is, employing $s_I$ shift vectors of the form

$$s_I = u_I \otimes e_z,$$  \hspace{1cm} (23)

with $u_I$ being a vector of length $N_p$ and $e_z = (0, 0, 1)^T$. From this choice of the $s_I$ vectors we obtain the fundamental equation

$$e_z^T \tilde{U}(\Omega)e_z = \cos \beta.$$  \hspace{1cm} (24)

Eq. (24) is employed throughout this work to derive analytical matrix elements for the overlap, kinetic, Coulomb, and angular momentum operators. For the matrix element of these operators we start from the analytical expressions derived for plain FECG by Cafiero and Adamowicz [40]. Conversely, angular momentum matrix elements are derived from the analytical expressions for plain FECG presented in our previous work [34]. The unprojected and analytically projected $z$-shifted floating explicitly correlated Gaussians are abbreviated with zFECG and apzFECG, respectively.

Given a quantum mechanical operator $\hat{O}$ commuting with the projector operator, the matrix element $IJ$ for apzFECG reads:

$$\mathcal{O}^{\text{apzFECG}}_{I,J[N,M,N,p]} = \langle \phi^{\text{apzFECG}}_I[N,M,N,p] | \hat{O} | \phi^{\text{apzFECG}}_J[N,M,N,p] \rangle = \langle \phi^{\text{FECG}}_I[N,M,N,p] | \hat{O} | \hat{P}^{[N,p]}_{M_N} \phi^{\text{FECG}}_J[N,M,N,p] \rangle,$$  \hspace{1cm} (25)

where the Hermiticity and idempotency of the projection operator, Eqs. (21)-(22), were exploited to simplify the integral expression. In the following, analytical matrix elements for a variety of quantum mechanical operators are derived. For the sake of brevity, the projection onto the parity states $\hat{P}^{[p]}_{C_I}$ has been omitted.
A. Overlap integral

The matrix elements of the identity operator for plain FECG is [40]

\[ \langle \phi^\text{FECG}_I | \phi^\text{FECG}_J \rangle = \tilde{S}_{IJ} \exp \left[ 2s_I^T A_I^{(r)} A_I^{-1} A_J^{(r)} s_J \right], \tag{26} \]

where

\[ \tilde{S}_{IJ} = \left( \frac{\pi N_p}{A_I^{(r)} + A_J^{(r)}} \right)^{\frac{1}{4}} \exp \left[ -s_I^T A_I^{(r)} s_I - s_J^T A_J^{(r)} s_J \right] \times \exp \left[ +s_I^T A_I^{(r)} A_I^{-1} A_J^{(r)} s_I + s_J^T A_J^{(r)} A_I^{-1} A_J^{(r)} s_J \right]. \tag{27} \]

In Eq. (26) we have separated \( \tilde{S}_{IJ} \) the term unaffected by the action of the rotation operator on the shift vector \( s_J \). The remaining term must be investigated since it involves the angular integration over the Euler angles. For apzFECG the overlap matrix element reads

\[ S_{\text{apzFECG}}^{IJ[N,M,p]} = \left\langle \phi^\text{apzFECG}_I(r; A_I^{(r)}, s_I) | \hat{P}_M^N \phi^\text{apzFECG}_J(r; A_J^{(r)}, s_J) \right\rangle, \tag{28} \]

and writing explicitly the projection operator leads to

\[ S_{\text{apzFECG}}^{IJ[N,M,p]} = \int \frac{d\Omega}{4\pi^3} D_{MN}^{[N]}(\Omega)^* \left\langle \phi_I(r; A_I^{(r)}, s_I) | \hat{P}_M^N \phi_J(r; A_J^{(r)}, U(\Omega)s_J) \right\rangle, \tag{29} \]

where we again drop the projector onto the parity state for the sake of brevity. Because \( \tilde{S}_{IJ} \) is invariant under the action of \( \hat{P}_M^N \), Eq. (29) can be written as

\[ S_{\text{apzFECG}}^{IJ[N,M,p]} = \tilde{S}_{IJ} \gamma_{MN}^N, \tag{30} \]

with

\[ \gamma_{MN}^N = \int \frac{d\Omega}{4\pi^3} D_{MN}^{[N]}(\Omega)^* \exp \left[ 2s_I^T A_I^{(r)} A_I^{-1} A_J^{(r)} U(\Omega)s_J \right]. \tag{31} \]

Since \( U(\Omega) = 1_{N_p} \otimes \tilde{U}(\Omega) \), we have

\[ U(\Omega)s_J = u_J \otimes \tilde{U}(\Omega)e_z, \tag{32} \]

where Eq. (23) and the definition of \( U(\Omega) \) in Eq. (16) have been exploited.

Considering Eqs. (23), (32), and (24) and that \( A_K^{(r)} = A_K^{(r)} \otimes 1_3 \) with \( k \in \{ I, J, IJ \} \), we have

\[ \exp \left[ 2s_I^T A_I^{(r)} A_I^{-1} A_J^{(r)} U(\Omega)s_J \right] = \exp \left[ C e_z^T \tilde{U}(\Omega)e_z \right] = \exp [C \cos \beta], \tag{33} \]
with $C$ given as
\[ C = 2 \mathbf{u}_I^T \bar{A}_I^{(r)} \bar{A}_{I J}^{-1} \bar{A}_J^{(r)} \mathbf{u}_J \, . \tag{34} \]

Finally, the angular integration reduces to
\[ \Upsilon_{M N}^N = \frac{1}{4 \pi^3} \int_0^{2 \pi} d\alpha \int_0^\pi d\beta \int_0^{2 \pi} d\gamma \sin(\beta) D_{M N}^{[N]^*}(\Omega) \exp[C \cos(\beta)] \, . \tag{35} \]

To analytically solve the triple integration over Euler angles, we first note that the elements $D_{00}^{[N]}(\beta)$ of the Wigner $D$-matrices corresponding to $M_N = 0$ are polynomial of $\cos \beta$ of degree $N$ with coefficients $a_\mu^{[N]}$ (e.g., $a_0^{[0]} = 1$, $a_0^{[1]} = 0$, $a_1^{[1]} = 1$),
\[ D_{00}^{[N]}(\Omega) = D_{00}^{[N]}(\beta) = \sum_{\mu=0}^{N} a_\mu^{[N]} (\cos \beta)^\mu \, . \tag{36} \]

Therefore, for apzFECG with $M_N = 0$, the integration over $\alpha$ and $\gamma$ Euler angles is trivial and Eq. (35) becomes
\[ \Upsilon_{M N}^N = \frac{1}{\pi} \sum_{\mu=0}^{N} \int_0^{\pi} \sin(\beta)(\cos(\beta))^\mu \exp[C \cos(\beta)] \, . \tag{37} \]

Furthermore, since apzFECG functions do not depend on Euler angles $\alpha$ and $\gamma$, the integration of the $D_{M_N M_N}^{[N]^*}(\Omega)$ yields zero for every $N \in \mathbb{N}_0$ and $M_N \neq 0$. The results of the integration over Euler angle $\beta$ in Eq. (37) for the spherically symmetric ground state as well as the two lowest rotationally excited states are then written as
\[ \Upsilon_{M N}^N = \begin{cases} \frac{2}{\pi C} \sinh(C) & N = 0, M_N = 0 \\ \frac{2}{\pi C} \cosh(C) - \frac{2}{\pi C^2} \sinh(C) & N = 1, M_N = 0 \\ \frac{2}{\pi C^3} \left[ (C^2 + 3) \sinh(C) - 3C \cosh(C) \right] & N = 2, M_N = 0 \\ 0 & \forall N \in \mathbb{N}_0, M_N \neq 0 \end{cases} \tag{38} \]

\textbf{B. Kinetic integral}

The kinetic integral for plain FECG reads [40]
\[ \langle \phi_{I}^{\text{FECG}} | - \nabla_T^T M \nabla_r | \phi_{J}^{\text{FECG}} \rangle = \tilde{S}_{I J} \left[ 4 (s_I - s_J) B(s_I - s_J) + 6 \text{Tr} \left( M \bar{A}_{I} \bar{A}_{I J}^{-1} \bar{A}_I \right) \right] \, . \tag{39} \]
where

\[ B = 4 A_J A^{-1}_{I,J} A_I M A_J A^{-1}_{I,J} A_I . \]  

(40)

For apzFECG it is

\[
T_{I J [N, M, p]}^{\text{apzFECG}} = \left\langle \phi_I | \hat{\rho}_{M N}^{[N,p]} | \phi_J \right\rangle = \tilde{S}_{I J} \Sigma^N_{M N},
\]

(41)

where the angular integral is written as

\[
\Sigma^N_{M N} = \int \frac{d\Omega}{4\pi^3} D^{[N]}_{M N M N} (\Omega)^* \exp [C \cos \beta] \\
\times \left[ -s_I B s_I - s_J B s_J + 2 s_I B U(\Omega) s_J + 6 \text{Tr} (M \bar{A}_J \bar{A}^{-1}_{I,J} \bar{A}_I) \right].
\]

(42)

We define

\[
\omega = -s_I B s_I - s_J B s_J + 6 \text{Tr} (M \bar{A}_J \bar{A}^{-1}_{I,J} \bar{A}_I),
\]

(43)

and

\[
\sigma = 2 u^T_I B u_J,
\]

(44)

so that Eq. (42) can be cast in the compact form

\[
\Sigma^N_{M N} = \int \frac{d\Omega}{4\pi^3} D^{[N]}_{M N M N} (\Omega)^* (\omega + \sigma \cos \beta) \exp [C \cos \beta],
\]

(45)

With Eq. (36), the integration over Euler angles can be reduced to the single integration over \( \beta \) for which these analytical results follow

\[
\Sigma^N_{M N} = \begin{cases} 
\frac{2}{\pi C^2} \left[ \sinh(C)(C \omega - \sigma) + C \sigma \cosh(C) \right] & N = 0, M_N = 0 \\
\frac{2}{\pi C^3} \left[ \sinh(C) ((C^2 + 2) \sigma - C \omega) + C \cosh(C)(C \omega - 2 \sigma) \right] & N = 1, M_N = 0 \\
\frac{2}{\pi C^4} \left[ \sinh(C) (C (C^2 + 3) \omega - (4C^2 + 9) \sigma) + C \cosh(C) ((C^2 + 9) \sigma - 3C \omega) \right] & N = 2, M_N = 0 \\
0 & \forall N \in \mathbb{N}_0, M_N \neq 0
\end{cases}.
\]

(46)

C. Coulomb integral

From Ref. [40] we retrieve the Coulomb matrix element for plain FECGs

\[
\left\langle \phi^\text{FECG}_I \left| \frac{1}{|r_i - r_j|} \right| \phi^\text{FECG}_J \right\rangle = \tilde{S}_{I J} \left( \frac{1}{S^T J_{ij} S} \right)^{\frac{1}{2}} \text{erf} \left[ \frac{S^T J_{ij} S}{\text{Tr} (J_{ij} A^{-1}_{I,J})} \right]^{\frac{1}{2}} ,
\]

(47)
where the vector $S$ is defined as

$$
S = A^{-1}_{IJ} (A_I s_I + A_J s_J) ,
$$

and

$$
J_{ij} = \begin{cases} 
E_{ii} & \text{if } i = j \\
E_{ii} + E_{jj} - E_{ij} - E_{ji} & \text{if } i \neq j 
\end{cases},
$$

with $(E_{ij})_{\alpha\beta} = \delta_{\alpha\beta}$ being an $N_p \times N_p$ matrix.

We now define the matrix elements for apzFECG functions as

$$
V_{apzFECG}^{IJ} = \langle \phi_I^{zFECG} | \frac{1}{|r_i - r_j|} \hat{P}_{MN}^{[N_p]} \phi_J^{zFECG} \rangle = \tilde{S}_{IJ} \Lambda_{MN}^N ,
$$

where

$$
\Lambda_{MN}^N = \int \frac{d\Omega}{4\pi^3} D_{MN.MN}^{[N]}(\Omega)^* e^C \cos \beta \left( \frac{1}{S^T J_{ij} S} \right)^{\frac{1}{2}} e^{\frac{1}{2} \text{erf} \left( \frac{\tau_{ij} + F_{ij} \cos \beta}{\text{Tr} (J_{ij} A^{-1}_{ij})} \right)} .
$$

Here, we adopt the notation of Cafiero and Adamowicz [40] corrected in order to account for the rotated $s_J$ vector

$$
\tilde{S} = A^{-1}_{IJ} (A_I s_I + A_J U(\Omega)s_J) .
$$

In order to make $\beta$ explicit and solve the angular integration, we consider the following substitution

$$
\tilde{S}^T J_{ij} \tilde{S} = \tau_{ij} + 2 s^T_I A_I A^{-1}_{IJ} J_{ij} A^{-1}_J U(\Omega) s_J = \tau_{ij} + F_{ij} \left( e^T_z \bar{U}(\Omega) e_z \right) = \tau_{ij} + F_{ij} \cos \beta ,
$$

with

$$
\tau_{ij} = s^T_I A_I A^{-1}_{IJ} J_{ij} A^{-1}_J A_I s_I + s^T_J A_J A^{-1}_{IJ} J_{ij} A^{-1}_J A_J s_J ,
$$

$$
F_{ij} = 2 \cdot u^T_J A_J A^{-1}_{IJ} J_{ij} A^{-1}_J A_J u_J .
$$

The angular integration in Eq. (51) is now written as

$$
\Lambda_{MN}^N = \int \frac{d\Omega}{4\pi^3} D_{MN.MN}^{[N]}(\Omega)^* e^C \cos \beta \left( \frac{1}{\tau_{ij} + F_{ij} \cos \beta} \right)^{\frac{1}{2}} e^{\frac{1}{2} \text{erf} \left( \frac{\tau_{ij} + F_{ij} \cos \beta}{\text{Tr} (J_{ij} A^{-1}_{IJ})} \right)} .
$$
While the integration with respect to $\alpha$ and $\gamma$ is trivial to integrate over $\beta \in [0, \pi)$, we change the variable, $y \equiv \tau_{ij} + F_{ij} \cos \beta$ so that Eq. (56) becomes

$$
\Lambda_{MN}^N = \frac{e^{-\tau_{ij}C}}{\pi F_{ij}} \int_{\tau_{ij} - F_{ij}}^{\tau_{ij} + F_{ij}} dy \ D_{M_{MN}}^N(y) \ y^{\frac{1}{2}} e^{\frac{C}{F_{ij}}} y \ erf \left( \left( \frac{y}{\text{Tr} (J_{ij} A_{ij}^{-1})} \right)^{\frac{1}{2}} \right) .
$$

(57)

To change the variable of the Wigner $D$-matrix we recall Eq. (36), namely that the elements $D_{00}^N(\beta)$ for any $N$ are polynomial of $\cos \beta$ of degree $N$. Therefore, after changing the variable, the zeroth diagonal element of the Wigner $D$-matrix can be written as

$$
D_{00}^N(y) = \sum_{\mu=0}^{N} a_{[N] \mu} \left( \frac{y - \tau_{ij}}{F_{ij}} \right)^{\mu} = \sum_{\mu=0}^{N} \sum_{k=0}^{\mu} \frac{\mu! a_{[N] \mu}}{(\mu - k)! k!} \left( -\frac{\tau_{ij}}{F_{ij}} \right)^{\mu-k} \left( \frac{1}{F_{ij}} \right)^k
$$

(58)

where in the second line the power of the binomial is written explicitly. By inserting Eq. (58), the polynomial form of the Wigner $D$-matrix, Eq. (57) reads

$$
\Lambda_{0}^N = \frac{e^{-\tau_{ij}C}}{\pi F_{ij}} \sum_{\mu=0}^{N} \sum_{k=0}^{\mu} \frac{\mu! a_{[N] \mu}}{(\mu - k)! k!} \left( -\frac{\tau_{ij}}{F_{ij}} \right)^{\mu-k} \left( \frac{1}{F_{ij}} \right)^k \times \int_{\tau_{ij} - F_{ij}}^{\tau_{ij} + F_{ij}} \ dy \ y^{-\frac{1}{2}+k} e^{\frac{C}{F_{ij}}} y \ erf \left( \left( \frac{y}{\text{Tr} (J_{ij} A_{ij}^{-1})} \right)^{\frac{1}{2}} \right),
$$

(59)

whereas expanding the exponential in a Taylor series yields

$$
\Lambda_{0}^N = \frac{e^{-\tau_{ij}C}}{\pi F_{ij}} \sum_{\mu=0}^{N} \sum_{k=0}^{\mu} \frac{\mu! a_{[N] \mu}}{(\mu - k)! k!} \left( -\frac{\tau_{ij}}{F_{ij}} \right)^{\mu-k} \left( \frac{1}{F_{ij}} \right)^k \times \sum_{n=0}^{\infty} \frac{1}{n!} \left( \frac{C}{F_{ij}} \right)^n \int_{\tau_{ij} - F_{ij}}^{\tau_{ij} + F_{ij}} \ dy \ y^{-\frac{1}{2}+k+n} \ erf \left( \left( \frac{y}{\text{Tr} (J_{ij} A_{ij}^{-1})} \right)^{\frac{1}{2}} \right),
$$

(60)

The integral over $y$ possesses an analytical solution,

$$
\Lambda_{0}^N = \frac{e^{-\tau_{ij}C}}{\pi F_{ij}} \sum_{\mu=0}^{N} \sum_{k=0}^{\mu} \frac{\mu! a_{[N] \mu}}{(\mu - k)! k!} \left( -\frac{\tau_{ij}}{F_{ij}} \right)^{\mu-k} \left( \frac{1}{F_{ij}} \right)^k \sum_{n=0}^{\infty} \frac{2}{(2k+2n+1)n!} \left( \frac{C}{F_{ij}} \right)^n \times \left[ - \text{erf}(\sqrt{F_{ij}}) (\tau_{ij} - F_{ij})^{k+n+\frac{1}{2}} + \text{erf}(\sqrt{F_{ij}}) (F_{ij} + \tau_{ij})^{k+n+\frac{1}{2}} + \frac{\text{Tr} (J_{ij} A_{ij}^{-1})^{k+n+\frac{1}{2}}}{\sqrt{\pi}} \left( \Gamma(k+n+1, t_1) - \Gamma(k+n+1, t_2) \right) \right],
$$

(61)
with
\[
  t_1 = \frac{\tau_{ij} + F_{ij}}{\text{Tr} \left( \bar{J}_{ij} A_{ij}^{-1} \right)},
\]
\[
  t_2 = \frac{\tau_{ij} - F_{ij}}{\text{Tr} \left( \bar{J}_{ij} A_{ij}^{-1} \right)}.
\]

If the resulting series in Eq. (61) is considered separately for each term, the first two can be evaluated exactly in terms of the lower incomplete Gamma function \( \gamma(n, b) \), while the latter is simplified according to the properties of the incomplete Gamma functions

\[
  \Lambda_0^N = e^{-\frac{\tau_{ij} C}{F_{ij}}} \sum_{\mu=0}^{N} \sum_{k=0}^{\mu} \frac{\mu! a_{\mu}^{[N]}}{(\mu - k)! k!} \left( -\frac{\tau_{ij}}{F_{ij}} \right)^{\mu-k} \left( \frac{1}{F_{ij}} \right)^{k}
\]
\[
  \left[ \left( -\frac{C}{F_{ij}} \right)^{-k+\frac{1}{2}} \text{erf}\left(\sqrt{t_1}\right) \gamma\left(k + \frac{1}{2} - \frac{C(F_{ij} + \tau_{ij})}{F_{ij}}\right) \right]
\]
\[
  - \left( -\frac{C}{F_{ij}} \right)^{-k+\frac{1}{2}} \text{erf}\left(\sqrt{t_2}\right) \gamma\left(k + \frac{1}{2} - \frac{C(F_{ij} - \tau_{ij})}{F_{ij}}\right)
\]
\[
  + \frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{\Gamma(k + n + 1, t_1, t_2)}{n! (2k + 2n + 1)} \left( \frac{C}{F_{ij}} \right)^n \text{Tr} \left( \bar{J}_{ij} A_{ij}^{-1} \right)^{k+n+\frac{1}{2}} \right],
\]

where the last remaining series converges factorially and only requires the generalized incomplete Gamma functions \( \Gamma(n, a, b) \), with \( n \in \mathbb{N}^+ \), that can be efficiently calculated in closed form as

\[
  \Gamma(n, t_1, t_2) = \Gamma(n) \left( e^{-t_1} \sum_{k=0}^{n-1} \frac{t_1^k}{k!} - e^{t_2} \sum_{k=0}^{n-1} \frac{t_2^k}{k!} \right).
\]

While Eq. (64) provides a general \( N \)-formula toward the calculation of Coulomb matrix elements, a closed formula can be obtained with the ‘differentiation under the integral’ technique from Eq. (59)

\[
  \Lambda_0^N = e^{-\frac{\tau_{ij} C}{F_{ij}}} \sum_{\mu=0}^{N} \sum_{k=0}^{\mu} \frac{\mu! a_{\mu}^{[N]}}{(\mu - k)! k!} \left( -\frac{\tau_{ij}}{F_{ij}} \right)^{\mu-k} \left( \frac{1}{F_{ij}} \right)^{k}
\]
\[
  \times 2 T^{\frac{1}{2}} F_{ij}^k \frac{\partial^k}{\partial C^k} \int_{\sqrt{(\tau_{ij} + F_{ij})/T}}^{\sqrt{(\tau_{ij} - F_{ij})/T}} dx \ e^{-\frac{C x^2}{F_{ij}}} \text{ erf } [x]
\]

with \( T = \text{Tr}(\bar{J}_{ij} A_{ij}^{-1}) \), the integration variable changed according to \( (y/T)^{\frac{1}{2}} = x \), and the \( k \)-th derivative with respect to \( C \) considered. The integral in Eq. (66) possesses an analytical solution,

\[
  \int_{a}^{b} dx \ e^{-q x^2} \text{ erf } [x] = 2 \sqrt{\frac{\pi}{q}} \left[ T \left( a \sqrt{2q}, \frac{1}{\sqrt{q}} \right) - T \left( b \sqrt{2q}, \frac{1}{\sqrt{q}} \right) \right],
\]

(67)
where $T(h, x)$ is the Owen’s T function.

**D. Squared total angular momentum expectation value**

To solve $\langle \Phi^z_{\text{FECG}} | \hat{\mathbf{N}}^2 | \Phi^z_{\text{FECG}} \rangle$, the squared total angular momentum expectation value for projected zFECG functions, we start from the matrix elements for FECGs derived in our previous work [34]

$$
\langle \phi^z_{\text{FECG}} | \hat{\mathbf{N}}^2 | \phi^z_{\text{FECG}} \rangle = \epsilon'_{ijk} \left[ 2 \left( s_I^T \omega_I^{(j,k)} A_{IJ}^{-1} \omega_I^{(j,k)} s_J \right) 4 \left( e^T A_{IJ}^{-1} \omega_I^{(j,k)} s_I \right) \right] S_{IJ}^{\text{FECG}},
$$

(68)

where $e = A_I s_I + A_J s_J$. Remember that for apzFECG functions, the vector $s_K$ ($K \in \{I, J\}$) must obey the constraint introduced in Eq. (23) and $s_J$ is subject to the rotation operator $\hat{R}(\Omega)$ involving the transformation matrix $U(\Omega)$. We recall [34] that

$$
\omega_{K}^{(x,y)} = \bar{A}_K \otimes (E_{xy} - E_{yx}) \quad \text{with} \quad K \in \{I, J\}.
$$

(69)

Considering Eqs. (23), (32), (24) and (69) we have

$$
\langle \phi^z_{\text{FECG}} | \hat{\mathbf{N}}^2 | \phi^{\text{apzFECG}}_{\text{zFECG}} \rangle = S_{IJ}^N \Xi_{MN}^N,
$$

(70)

where

$$
\Xi_{MN}^N = \epsilon'_{ijk} \int \frac{d\Omega}{4\pi^3} D_{MN}^{[N]}(\Omega)^* e^C \cos^3 \beta
$$

$$
\left[ 2(\mathbf{u}_I \bar{A}_I \mathbf{u}_I) (\mathbf{e}_z^T (E_{jk} - E_{kj}) U(\Omega) \mathbf{e}_z) + 4 \left( (\mathbf{u}_I \bar{A}_I \mathbf{u}_I) (\mathbf{e}_z^T (E_{jk} - E_{kj}) \bar{U}(\Omega) \mathbf{e}_z) \right) + (\mathbf{u}_J \bar{A}_J \mathbf{u}_J) (\mathbf{e}_z^T \bar{U}(\Omega) (E_{jk} - E_{kj}) \bar{U}(\Omega) \mathbf{e}_z) \right]
$$

$$
\times \left[ (\mathbf{u}_I \bar{A}_I \mathbf{u}_I) (\mathbf{e}_z^T (E_{jk} - E_{kj}) \mathbf{e}_z) + (\mathbf{u}_J \bar{A}_J \mathbf{u}_J) (\mathbf{e}_z^T \bar{U}(\Omega) (E_{jk} - E_{kj}) \mathbf{e}_z) \right],
$$

(71)

where $C$ has been defined in Eq. (34).
Furthermore, provided that \((j, k) \in \{(2, 3), (3, 1), (1, 2)\}\) (see Ref. [34] for a detailed demonstration), it is

\[
e^T_z (E_{23} - E_{32}) e_z = \cos \beta ,
\]

\[
e^T_z (E_{31} - E_{13}) e_z = \cos \beta ,
\]

\[
e^T_z (E_{23} - E_{32}) e_z = + \sin \alpha \sin \beta ,
\]

\[
e^T_z (E_{31} - E_{13}) e_z = - \cos \alpha \sin \beta ,
\]

\[
e^T_z U(\Omega)^T (E_{23} - E_{32}) U(\Omega) e_z = 0 ,
\]

\[
e^T_z U(\Omega)^T (E_{31} - E_{13}) U(\Omega) e_z = 0 ,
\]

\[
e^T_z (E_{23} - E_{32}) e_z = 0 ,
\]

\[
e^T_z (E_{31} - E_{13}) e_z = 0 ,
\]

\[
e^T_z U(\Omega)^T (E_{23} - E_{32}) e_z = - \sin \alpha \sin \beta ,
\]

\[
e^T_z U(\Omega)^T (E_{31} - E_{13}) e_z = + \cos \alpha \sin \beta ,
\]

while it can be shown that for \((j, k) = (1, 2)\) all these expressions evaluate to zero.

Eq. (71) can now be written as

\[
\Xi^{N}_{MN} = \int \frac{d\Omega}{4\pi^2} D_{MN}^{[N]}(\Omega) \ast e^C \cos \beta \\
\quad \times \left[ 2(C \cos \beta) + (C \sin \alpha \sin \beta)(-C \sin \alpha \sin \beta) \\
\quad + (-C \cos \alpha \sin \beta)(C \cos \alpha \sin \beta) \right],
\]

and its analytical solution to the angular integration for \(N = 0, 1, 2\) yields

\[
\Xi^{N}_{MN} = \begin{cases} 
0 & \text{if} \ N = 0, M_N = 0 \\
2 \ U_0^1 & \text{if} \ N = 1, M_N = 0 \\
6 \ U_0^2 & \text{if} \ N = 2, M_N = 0 \\
0 & \forall N \in \mathbb{N}_0, M_N \neq 0
\end{cases},
\]

where \(U_{MN}^N\) are the solution of the overlap angular integration given in Eq. (38). This is in accordance with the expected eigenvalue for the squared total spatial angular momentum \(N(N + 1)\) in Hartree atomic units.
E. Projection of the angular momentum onto the $z$ axis

We recall the $\langle \hat{N}_z \rangle_{IJ}$ matrix elements for FECG functions [34]

$$\langle \phi_I^{\text{FECG}} | \hat{N}_z | \phi_J^{\text{FECG}} \rangle = \frac{2}{i} \left( e^T A^{-1} \omega_{(1,2)}^{(1,2)} s_J \right) \langle \phi_I | \phi_J \rangle .$$

(84)

Here, we cannot simplify the expectation value for apzFECG since $[\hat{R}(\Omega), \hat{N}_z] \neq 0$. The term in parenthesis then becomes

$$e^T A^{-1} \omega_{(1,2)}^{(1,2)} s_J = s_I A_I A^{-1} \omega_{(1,2)}^{(1,2)} s_J + s_J A_J A^{-1} \omega_{(1,2)}^{(1,2)} s_J$$

$$= (u_I \bar{A}_I \bar{A}^{-1} \bar{A}_J u_J) \left( e^T \tilde{U}(\Omega') (E_{21} - E_{12}) \tilde{U}(\Omega) e_z \right)$$

$$+ (u_J \bar{A}_J \bar{A}^{-1} \bar{A}_J u_J) \left( e^T \tilde{U}(\Omega)^T (E_{21} - E_{12}) \tilde{U}(\Omega) e_z \right) = 0 .$$

(85)

The latter term $e^T \tilde{U}(E_{21} - E_{12}) \tilde{U}(\Omega) e_z = 0$ from Eqs. (76)-(77), while the former one is

$$e^T \tilde{U}(\Omega') (E_{21} - E_{12}) \tilde{U}(\Omega) e_z = \cos \alpha' \sin \alpha \sin \beta \sin \beta' - \cos \alpha \sin \alpha' \sin \beta \sin \beta'.$$

(86)

The resulting expectation value on apzFECG functions reads

$$\langle \phi_I^{\text{apzFECG}} | \hat{N}_z | \phi_J^{\text{apzFECG}} \rangle = \tilde{S}_{IJ} \int \frac{d\Omega}{4\pi^3} \int \frac{d\Omega'}{4\pi^3} D_{MN}^{[N]}(\Omega')^* D_{MN}^{[N]}(\Omega)^* \exp [C \cos \beta]$$

$$\times \left( u_I \bar{A}_I \bar{A}^{-1} \bar{A}_J u_J \right) \left[ \sin(\alpha - \alpha')(\sin \beta)^2(\sin \beta')^2 \right] ,$$

(87)

that evaluates to zero for every $N$, $M_N$ pairs

$$\langle \phi_I^{\text{apzFECG}} | \hat{N}_z | \phi_J^{\text{apzFECG}} \rangle = 0 \quad \forall N \mid N = (0, 1, 2, \ldots), M_N = (-N, \ldots, +N) .$$

(88)

F. Elimination of center-of-mass contamination

Contributions from the center of mass are eliminated from the expectation values according to the protocol devised in Ref. [37]. First, the variational matrices $A^{(r)}$ and variational vectors $s^{(r)}$ are transformed to a given TICC, $A^{(x)}$ and $s^{(x)}$, respectively, and defined in block diagonal form

$$A^{(r)}_I = U_x^{-T} \begin{pmatrix} A^{(x)}_I & 0 \\ 0 & c_{AI} \end{pmatrix} U_x^{-1} ,$$

(89)

$$s^{(r)} = U_x \begin{pmatrix} S^{(x)} \\ c_{SI} \end{pmatrix} ,$$

(90)
where the $N_p - 1 \times N_p - 1$ matrix $A^{(r)}_I$ and the $N_p - 1$ vector $S^{(x)}$ are related to the internal coordinates, while $c_{AI}$ and $c_{SI}$ are scalar parameters associated to the center of mass. Note the superscript distinguishing the LFCC set ($r$) from a generic TICC set ($x$). Although the choice of zero for both $c_{AI}$ and $c_{SI}$ for each $I \in \{1, \ldots, N_b\}$ would systematically cancel center-of-mass contributions from every expectation value, $c_{AI} = 0$ leads to a singular matrix $A_I$, which violates the square-integrable and positive-definiteness requirements for the basis functions. Ref. [37] defined a rigorous approach to handle the $c_A$-dependent terms without violating both these requirements. Here, we apply this approach for the apzFE CGs analytical matrix elements for which center-of-mass contributions must be subtracted.

The only center-of-mass dependent term arising in the analytical kinetic energy integral with the favorable choice $c_{SI} = 0$, is the $R$ term defined as

$$ R = \text{Tr} \left( M A^{(r)}_I A^{-1}_{IJ} A^{(r)}_J \right). \tag{91} $$

The translational contamination can now be eliminated by replacing

$$ R_{\text{corr.}} = R - \frac{1}{4} c_{AI} c_M, \tag{92} $$

with $c_M = \sum_{i=0}^{N_p} m_i$ being the total mass of the system. We emphasize that minimization of the energy with respect to translationally invariant parameters only excludes the center-of-mass coordinate, and hence, reduces the original problem for $N_p$ particles to a simpler optimization problem for $N_p - 1$ pseudo-particles with lower complexity.

G. Numerical stability

We investigate the numerical stability of the analytical matrix elements in finite-precision arithmetic. A naive implementation of the integral expressions results in ill-conditioned overlap and Hamiltonian matrices because of the hyperbolic functions. To restore numerical stability, we introduce normalization for the basis functions, defined as

$$ \Phi_{I[N,M_N,p]}^{\text{apzFE CG}} = \frac{\hat{\Phi}_{I[N,M_N,p]}^{\text{apzFE CG}}}{|\Phi_{I[N,M_N,p]}^{\text{apzFE CG}}|}, \tag{93} $$

where the normalization factor is

$$ |\Phi_{I[N,M_N]}| = \langle \hat{P}_{M_N}^{[N,p]} \phi_{I[N,M_N,p]}^{\text{apzFE CG}} \rangle_{\hat{P}_{M_N}^{[N,p]} \phi_{I[N,M_N,p]}^{\text{apzFE CG}}}^{1/2}. \tag{94} $$

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Matrix elements $\mathcal{O}_{IJ}^{\text{apzFECG}}$ for a generic operator $\hat{O}$ are then evaluated as

$$\langle \Phi_{I[N,M,N,p]}^{\text{apzFECG}} | \hat{O} | \Phi_{J[N,M,N,p]}^{\text{apzFECG}} \rangle = \frac{\langle \hat{P}_{I[N,M,N,p]}^{\text{apzFECG}} | \hat{O} | \hat{P}_{J[N,M,N,p]}^{\text{apzFECG}} \rangle}{|| \Phi_{I[N,M,N,p]}^{\text{apzFECG}} || || \Phi_{J[N,M,N,p]}^{\text{apzFECG}} ||}. \quad (95)$$

Although the normalization of apzFECGs assures well-conditioned representation matrices for the quantum mechanical operators, extreme $C$ values cause overflow of the hyperbolic sine and cosine functions as well as cancellation errors in the kinetic energy terms because of the high powers of $C$. To remedy these two sources of errors, we differentiate the integral evaluation scheme for different orders of magnitude of $C$ by allowing higher-precision arithmetic to be employed when needed. In particular, we detected possible sources of numerical instabilities for $|C| > 700$ when working in double precision floating point arithmetic. However, quadruple precision suffices for achieving the desired accuracy for every test calculations with unconstrained optimization of the variational parameters. While basis functions yielding $|C| > 700$ can also be discarded, we prefer the latter strategy to keep the energy function continuous with respect to the variational parameters.

**VI. NUMERICAL RESULTS**

The formulae derived have been implemented in a C++ computer program. These analytical expressions allow us to calculate matrix elements reliably. Other sources of error such as numerical integration or truncation of infinite series are eliminated by our approach.

As test examples for the novel basis function presented in this work we chose the dihydrogen molecular ion, $H_2^+=\{p^+,p^+,e^-\}$, and dihydrogen, $H_2=\{p^+,p^+,e^-e^-\}$ treated explicitly as three and four particle systems, respectively. The Born-Oppenheimer approximation is not invoked, i.e., nuclei and electrons are described on equal footing. The energies obtained for the first three rotational states are shown in Tables I and II, respectively. For each state, we optimized a different basis sets consisting of 400 and 600 zFECG functions, respectively. Matrix elements were calculated as discussed in Sec. V where the projection operator was applied to the ket function. The virial coefficient, $\eta = |1 + \langle \Psi | \hat{V} | \Psi \rangle / (2 \langle \Psi | \hat{T} | \Psi \rangle)|$ vanishes for the exact solution [35], so that it represents a diagnostic for the overall quality of the variationally optimized wave function. The basis set size was gradually increased following the competitive selection method [35] for which the newer basis functions entering the basis set are selected from a large pool of randomly generated trial functions. A simultaneous
refinement of the non-linear variational parameters was crucial to achieve efficient energy convergence. This optimization problem of minimizing the energy with respect to the set of non-linear parameters is a difficult problem as the objective function is non-convex, non-separable, and often (Sec. V G) ill-conditioned. We relied on two derivative-free algorithms: the Subplex algorithm by Rowan [41] and the Principal Axis method discussed by Brent [42]. In our computer implementation of both methods, we used the NLopt package [43]. We employed our multi-channel optimization approach presented in our previous work [37] and we have included every possible set of Jacobi coordinates, heavy-particle-centered (HPC) coordinates as well as the center-of-mass-centered coordinates. The construction of the Gaussian parameters through different $U^\text{TICC}_a$ maps allows us to explore the parameter space faster and to describe different groupings of the particles with the most appropriate TICC set. The optimized basis-function parameters are deposited in the supplementary material. Investigating the results in Table I, we observe that the energies are well converged with the number of basis functions.

### TABLE I: Nonrelativistic energies of $H^+_2 = \{p^+,p^+,-e\}$, compared with results from Ref. [44] in the last column. The calculations include all possible Jacobi coordinates, the heavy-particle-centered, and the center-of-mass-centered coordinate sets.

| $N$ | $\langle \hat{H} \rangle / E_h \ (N_b = 400)$ | $\eta$ | $\langle \hat{H} \rangle_{\text{Ref.}} / E_h \ (N_b = 4000)$ | $^a\delta E / nE_h$ |
|-----|---------------------------------|--------|---------------------------------|------------------|
| 0   | -0.597139062111                 | $10^{-9}$ | -0.597139063079                | -0.968           |
| 1   | -0.596873736772                | $10^{-9}$ | -0.596873738784                | -2.012           |
| 2   | -0.596345204133                | $10^{-9}$ | -0.596345205489                | -1.356           |

$$^a\delta E = E(\text{Ref.}) - \langle \hat{H} \rangle$$

### VII. CONCLUSIONS

Projection techniques increase the effectiveness of variational basis function optimization carried out in the desired eigenspace. The formalism developed in this paper analytically solves the projection based approach for the subset of explicitly correlated floating Gauss-
TABLE II: Nonrelativistic energies of \( H_2 = \{ p^+, p^+, e^- \} \), compared with results from Ref. [45] in the last column. The calculations include all possible Jacobi coordinates, the heavy-particle-centered, and the center-of-mass-centered coordinate sets.

| \( \langle \hat{H} \rangle / E_h (N_b = 600) \) | \( \eta \) | \( \langle \hat{H} \rangle_{\text{Ref.}} / E_h (N_b = 4200) \) | \( ^a \delta E/nE_h \) |
|----------------|-----|----------------|----------------|
| \( N = 0 \)     | \( -1.16402502482 \times 10^{-8} \) | \( -1.164025031 \) | \( -6.18 \) |
| \( N = 1 \)     | \( -1.16348516709 \times 10^{-8} \) | \( -1.163485173 \) | \( -5.91 \) |
| \( N = 2 \)     | \( -1.16241040566 \times 10^{-7} \) | \( -1.162410409 \) | \( -3.34 \) |

\(^a \delta E = E(\text{Ref.}) - \langle \hat{H} \rangle\)

sions having shift vectors aligned on one axis. We have derived analytical expressions of important matrix elements for projected zFECGs with arbitrary angular momentum and parity configurations. The numerical examples presented demonstrate the correctness of the derived formulae and the applicability of the approach to excited rotational states of small molecules.

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