Analytically projected, rotationally symmetric, explicitly correlated Gaussian functions with one-axis-shifted centers

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An 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. Muolo, E. Mátyus, and M. Reiher, J. Chem. Phys. **149**, 184105 (2018)], to explicitly correlated Gaussian functions 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 formalism can be used as a unified framework for high-accuracy calculations of properties of small atoms and molecules.

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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 interparticle distances [1–18]. Nonseparable 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 [12,19–23] that explicitly include powers of the interelectronic distances $r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$. However, the difficulties of the analytical calculation of their matrix elements prevent application of this approach to larger systems [24–26]. Generality with respect to the particle number and accessible analytical Hamiltonian matrix elements are achievable through powers of the quadratic form of the interparticle distances that define explicitly correlated Gaussian-type (ECG) functions [1,2]. Plain explicitly correlated Gaussian (pECG) functions for N_p interacting particles,

$$\phi_I^{\mathrm{pECG}} = \exp\left[-\sum_{i<j=1}^{N_p} A_{Iij}\boldsymbol{r}_i\cdot\boldsymbol{r}_j\right], \tag{1}$$

are the simplest functions of this type and have been successfully employed to describe a number of diverse physical systems, from small atoms and molecules to light nuclei, hadrons, quantum dots, and Efimov systems [15,17,27]. pECG functions are also manifestly spherically symmetric, i.e., invariant under rotation, as they are eigenfunctions of the total angular momentum squared operator with eigenvalue zero. Additional and important higher angular momentum contributions originate from the cross terms of the exponential part, i.e., $\exp(-A_{Iij}\boldsymbol{r}_i\cdot\boldsymbol{r}_j)$, which, when expanded into a power series, contain terms of the form

$$(\boldsymbol{r}_i\cdot\boldsymbol{r}_j)^n = \sum_{2k+l=n}\frac{4\pi(2k+l)!}{2^k k!(2k+2l+1)!!}|r_i|^{2k}|r_j|^{2k} \times\sum_{m=-l}^{l}\mathcal{Y}_{lm}(\boldsymbol{r}_i)\mathcal{Y}_{lm}(\boldsymbol{r}_j), \tag{2}$$

which are associated with different solid spherical harmonics $\mathcal{Y}_{lm}$ for the coordinates $\boldsymbol{r}_i$ and $\boldsymbol{r}_j$.

Although these advantages made ECG-type functions very popular in high-accuracy calculations [3,5,11,13,14,28], the spherical symmetry limits the applicability of plain ECGs to ground rotational states only. Different approaches [27,29] have been developed to extend ECGs to nonspherical problems, i.e., for calculating states with nonzero total spatial angular momentum quantum numbers N.

In general, the ECGs are being multiplied with a nonspherical function, $\theta_{NM_N}(\boldsymbol{r})$, of the collective position vectors $\boldsymbol{r}$ that for one particle in a central potential would just reduce to a solid spherical harmonic, $\mathcal{Y}(\boldsymbol{r}_1)$. The generalization to the N_p-particle case is a vector-coupled product of the solid spherical harmonics of the relative coordinates,

$$\theta_{NM_N}(\boldsymbol{r}) = \sum_{\kappa=\{m_1,m_2,\ldots,m_{N_p}\}}\mathcal{C}_\kappa\prod_{i=1}^{N_p}\mathcal{Y}_{l_i m_i}(\boldsymbol{r}_i), \tag{3}$$

where $\mathcal{C}_\kappa$ is a product of Clebsch-Gordan coefficients,

$$\begin{aligned}\mathcal{C}_\kappa = {}& \langle l_1 m_1 l_2 m_2|L_{12}m_1+m_2\rangle \\ & \times\langle L_{12}m_1+m_2 l_3 m_3|L_{123}m_1+m_2+m_3\rangle \\ & \cdots\langle L_{12\ldots N_p-1}m_1+m_2+\cdots+m_{N_p-1}l_{N_p}m_{N_p}|NM_N\rangle,\end{aligned} \tag{4}$$

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that couples the orbital angular momenta sequentially to the specified total quantum numbers (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 $(l_1, l_2, \ldots, l_{N_p}; L_{12}, L_{123}, \ldots)$ weighted by $\mathcal{C}_\kappa$. Equation (3) is a partial-wave expansion whose direct implementation is cumbersome since the matrix elements for this choice of $\theta_{NM_N}(\boldsymbol{r})$ 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. [30–34] focused on ECG functions specifically tailored for $N = 1$ states considering the sets of orbital angular momenta $(l_1 = 0, \ldots, l_i = 1, \ldots, l_{N_p} = 0)$. References [35–38] tackled $N = 2$ states analogously with lowest-order angular momentum couplings.

Alternatively, representations of $\theta_{NM_N}(\boldsymbol{r})$, including the orientation of a global vector $\boldsymbol{v}$ formed as a linear combination of all particle coordinates $\{\boldsymbol{r}_i\}$, have been successfully employed in high-accuracy calculations of properties of small atoms and molecules [15,39]. This approach is based on an equivalence condition between the global vector representation of $\theta_{NM_N}(\boldsymbol{r})$ 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 $\theta_{NM_N}(\boldsymbol{r})$ can be represented. These alternative formulations are strictly derived from the partial-wave expansion as a result of having truncated or variationally approximated Eq. (3).

In this work, we extend our numerical projection scheme onto irreducible representations of the rotational-inversion O(3) group presented in our previous work [40], focusing on a special case where the integral projector can now be solved analytically. In Ref. [40], we considered explicitly correlated Gaussian functions with centers shifted by a vector in the three-dimensional Euclidean space, $\boldsymbol{s} \in \mathbb{R}^3$. 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 functional form by studying the first three rotational states of the dihydrogen molecular ion $H_2{}^+ = \{p^+, p^+, e^-\}$ treated explicitly as a three-particle system and the dihydrogen molecule $H_2 = \{p^+, p^+, e^-, e^-\}$ treated explicitly as a four-particle system.

II. THEORY

We consider a nonrelativistic Coulombic Hamiltonian for N_p particles,

$$\hat{H}_{\text{lab}} = -\boldsymbol{\nabla}_{\boldsymbol{r}}^T M \boldsymbol{\nabla}_{\boldsymbol{r}} + \sum_{i=1}^{N_p} \sum_{j>i}^{N_p} \frac{q_i q_j}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}, \tag{5}$$

with the position vector $\boldsymbol{r}_i$ of the ith particle in the laboratory-fixed Cartesian coordinates (LFCC), its mass m_i, and its charge q_i. $\boldsymbol{\nabla}_{\boldsymbol{r}}$ is the gradient with respect to $\boldsymbol{r}_i$, and M is an $N_p \times N_p$ matrix with elements $M_{ij} = \delta_{ij}/2m_i$.

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

$$U_x \boldsymbol{r} = \left(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_{N_p-1}, \boldsymbol{x}_{\text{CM}}\right)^T, \tag{6}$$

in which the $\boldsymbol{x}_{\text{CM}} = \sum_{i=1}^{N_p} m_i \boldsymbol{r}_i / (\sum_{i=1}^{N_p} m_i)$ are the center-of-mass Cartesian coordinates and $\boldsymbol{x} \equiv (\boldsymbol{x}_1, \ldots, \boldsymbol{x}_{N_p-1})$ denotes the translationally invariant Cartesian coordinates (TICC) corresponding to the internal coordinates of the system generated through the relative tranformation matrix U_x. A transformation of the Hamiltonian in Eq. (5) separates the kinetic energy term for the center of mass from the internal Hamiltonian [27,41]:

$$\hat{H}_{\text{int}} = -\boldsymbol{\nabla}_{\boldsymbol{x}}^{\text{T}} \mu \boldsymbol{\nabla}_{\boldsymbol{x}} + \sum_{i=1}^{N_p-1} \sum_{j>i}^{N_p-1} \frac{q_i q_j}{|(\boldsymbol{f}_{ij} \otimes \mathbb{1}_3)\boldsymbol{x}|}, \tag{7}$$

where

$$\mu = U_x^{-T} M U_x \tag{8}$$

and

$$(\boldsymbol{f}_{ij})_k = \left(U_x^{-1}\right)_{ik} - \left(U_x^{-1}\right)_{jk}. \tag{9}$$

This separation of the center-of-mass coordinate requires transforming both the Hamiltonian and the state function and has been exploited in practice [14,15].

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 [42,43]. 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 algebraically 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 representation is expanded as a linear combination of (anti-)symmetrized floating explicitly correlated Gaussian (FECG) functions:

$$\Psi(\mathbf{r}) = \sum_{I=1}^{N_b} c_I \, \boldsymbol{\chi}_I^{S,M_S} \hat{Y} \phi_I^{\mathrm{FECG}}\left(\boldsymbol{r}; A_I^{(r)}, \boldsymbol{s}_I^{(r)}\right), \tag{10}$$

where c_I are the expansion coefficients, $\boldsymbol{\chi}_I^{S,M_S}$ 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 [44]. FECGs have the following general form:

$$\phi_I^{\mathrm{FECG}}\left(\boldsymbol{r}; A_I^{(r)}, \boldsymbol{s}_I^{(r)}\right) = \exp\left[-\left(\boldsymbol{r}-\boldsymbol{s}_I^{(r)}\right)^T \left(A_I^{(r)} \otimes \mathbb{1}_3\right)\left(\boldsymbol{r}-\boldsymbol{s}_I^{(r)}\right)\right]. \tag{11}$$

Here, $A_I^{(r)}$ is an $N_p \times N_p$ symmetric matrix of which the $\frac{1}{2}N_p(N_p+1)$ elements are variational parameters, with the subscript I indicating that the matrix is unique for each basis function and the superscript indicating that the variational parameters refer to the LFCC set. It is $\boldsymbol{r}(A_I^{(r)} \otimes \mathbb{1}_3)\boldsymbol{r} > 0 \;\forall\; \boldsymbol{r} \in \mathbb{R}^{3N_p}$; that is, $A_I^{(r)}$ must be positive definite to ensure square integrability of the $\phi_I^{[\mathrm{FECG}]}$ basis function. A necessary and sufficient condition for a symmetric real matrix to be positive definite is that all eigenvalues must be positive. Here $\boldsymbol{r}-\boldsymbol{s}_I^{(r)}$ stands for a set of vectors $\{\boldsymbol{r}_1-\boldsymbol{s}_{I1}^{(r)}, \ldots, \boldsymbol{r}_{N_p}-\boldsymbol{s}_{IN_p}^{(r)}\}$ that correspond to shifted particle coordinates with the $3N_p$-dimensional vector $\boldsymbol{s}_I^{(r)}$ composed of parameters to be optimized in a variational procedure.

Note that the floating spherical Gaussian orbitals approach introduced by Frost in 1967 [45] is based on one-particle functions (orbitals) and is therefore a limiting case of our approach for diagonal (and not dense) Gaussian parameter matrices A_I. In fact, this special case reduces our FECG basis functions to a product of exponential functions, each of which being spherically symmetric about its origin. By contrast, FECG basis functions with dense A_I Gaussian parameter matrices include partial-waves contribution from many higher angular momentum states (see the Introduction).

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

IV. PROJECTION TECHNIQUE

The FECGs in Eq. (11) define Gaussian functions with shifted centers to allow for suitable deformations of the ansatz for the all-particle wave function that are predominantly needed for polyatomic systems [27,43]. A general FECG function is, however, neither an eigenfunction of the squared total angular momentum operator $\boldsymbol{N}^2$ nor an eigenfunction of the space-inversion operator $\hat{p}$. As the rotation-inversion symmetry must be restored variationally in the limit of a complete basis set, these basis functions give rise to poor energy convergence.

To alleviate this problem, we recently proposed an integral projection operator, $\hat{P}_{M_N}^{[N,p]}$ [40], 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:

$$\hat{P}_{M_N}^{[N,p]} = \hat{P}_{M_N M_N}^{[N]} \hat{P}_{C_I}^{[p]}, \tag{12}$$

with

$$\hat{P}_{M_1M_2}^{[N]} = \int \frac{d\Omega}{4\pi^3} \, D_{M_1M_2}^{[N]}(\Omega)^* \hat{R}(\Omega) \tag{13}$$

and

$$\hat{P}_{C_I}^{[p]} = \hat{\mathcal{E}} + p \cdot \hat{\mathcal{I}}, \tag{14}$$

where $\hat{\mathcal{E}}$ is the identity operator, $\hat{\mathcal{I}}$ is the spatial inversion operator, and $D_{M_1M_2}^{[N]}$ is the element of the Nth Wigner D matrix,

$$D_{M_1M_2}^{[N]} = \exp(-iM_1\alpha)\, d_{M_1M_2}^{[N]}(\beta) \exp(-iM_2\gamma), \tag{15}$$

with the Wigner (small) d matrix being

$$d_{M_1M_2}^{[N]}(\beta) = \left[(N+M_1)!(N-M_1)!(N+M_2)!(N-M_2)!\right]^{\frac{1}{2}} \times \sum_s \left[\frac{(-1)^{M_1-M_2+s}\left(\cos\frac{\beta}{2}\right)^{2N+M_2-M_1-2s}\left(\sin\frac{\beta}{2}\right)^{M_1-M_2+2s}}{(N+M_2-s)!s!(M_1-M_2+s)!(N-M_1-s)!}\right]. \tag{16}$$

$\hat{R}(\Omega)$ is the quantum-mechanical rotation operator over the Euler angles $\Omega \equiv \{\alpha, \beta, \gamma\}$ [46],

$$\hat{R}(\alpha, \beta, \gamma) = \exp(-i\alpha N_z) \exp(-i\beta N_y) \exp(-i\gamma N_z). \tag{17}$$

The effect of the projector operator in Eq. (12) on a state $|N\, M_N\rangle$ is

$$\hat{P}_{M_1M_2}^{[N_1]} |N_2M_2\rangle = |N_1M_1\rangle\, \delta_{N_1N_2}\, \delta_{M_1M_2}, \tag{18}$$

with $|NM_N\rangle$ being angular momentum eigenstates. Note that our original implementation [40] 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 an analytical expression can be derived.

The form of the rotation operators in Eq. (17) 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:

$$\begin{aligned}\hat{R}(\Omega)\phi_I^{\mathrm{FECG}}\left(\boldsymbol{r};A_I^{(r)},\boldsymbol{s}_I^{(r)}\right) &= \phi_I^{\mathrm{FECG}}\left(U(\Omega)^{-1}\boldsymbol{r};A_I^{(r)},\boldsymbol{s}_I^{(r)}\right)\\ &= \exp\left[-\left(U(\Omega)^{-1}\boldsymbol{r}-\boldsymbol{s}_I^{(r)}\right)^T\left(\bar{A}_I^{(r)}\otimes\mathbb{1}_3\right)\left(U(\Omega)^{-1}\boldsymbol{r}-\boldsymbol{s}_I^{(r)}\right)\right]\\ &= \exp\left[-\left(\boldsymbol{r}-U(\Omega)\boldsymbol{s}_I^{(r)}\right)^T\left(\bar{A}_I^{(r)}\otimes\tilde{U}(\Omega)^{-T}\tilde{U}(\Omega)^{-1}\right)\left(\boldsymbol{r}-U(\Omega)\boldsymbol{s}_I^{(r)}\right)\right]\\ &= \phi_I^{\mathrm{FECG}}\left(\boldsymbol{r};A_I^{(r)},U(\Omega)\boldsymbol{s}_I^{(r)}\right),\end{aligned} \tag{19}$$

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

$$\tilde{U}(\Omega)=\begin{pmatrix}\cos\alpha\cos\beta\cos\gamma-\sin\alpha\sin\gamma & -\cos\gamma\sin\alpha-\cos\alpha\cos\beta\sin\gamma & -\cos\alpha\sin\beta\\ \cos\beta\cos\gamma\sin\alpha+\cos\alpha\sin\gamma & \cos\alpha\cos\gamma-\cos\beta\sin\alpha\sin\gamma & -\sin\alpha\sin\beta\\ \cos\gamma\sin\beta & \sin\beta\sin\gamma & \cos\beta\end{pmatrix}. \tag{20}$$

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

$$[\hat{R}(\Omega),\hat{H}\,] = 0, \tag{21}$$

$$[\hat{R}(\Omega),\hat{N}^2] = 0, \tag{22}$$

$$[\hat{R}(\Omega),\hat{N}_z] \neq 0, \tag{23}$$

$$[\hat{R}(\Omega),\hat{p}\,] = 0. \tag{24}$$

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

$$\left(\hat{P}^{[N]}_{M_NM_N}\right)^2=\hat{P}^{[N]}_{M_NM_N} \tag{25}$$

$$\left(\hat{P}^{[N]}_{M_NM_N}\right)^\dagger=\hat{P}^{[N]}_{M_NM_N}. \tag{26}$$

Properties in Eqs. (21)–(26) are employed in the remainder of this work for the calculation of quantum-mechanical expectation values.

V. MATRIX ELEMENTS

In this section, we present analytically projected FECGs matrix elements for important operators in the special case of unidimensional shift vectors, that is, employing $\boldsymbol{s}_I$ shift vectors of the form

$$\boldsymbol{s}_I^{(r)}=\boldsymbol{u}_I^{(r)}\otimes\boldsymbol{e}_z, \tag{27}$$

where $\boldsymbol{u}_I^{(r)}$ is a vector of length N_p and $\boldsymbol{e}_z=(0,0,1)^T$. From this choice of the $\boldsymbol{s}_I^{(r)}$ vectors we obtain the fundamental relation

$$\boldsymbol{e}_z^T\tilde{U}(\Omega)\boldsymbol{e}_z=\cos\beta. \tag{28}$$

Equation (28) 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 FECGs by Cafiero and Adamowicz [47]. Conversely, angular momentum matrix elements are derived from the analytical expressions for plain FECGs presented in our previous work [40]. The unprojected and analytically projected z-shifted floating explicitly correlated Gaussian functions are abbreviated with zFECGs and apzFECGs, respectively.

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

$$\begin{aligned}\mathcal{O}^{\mathrm{apzFECG}}_{IJ[N,M_N,p]} &= \left\langle\phi^{\mathrm{apzFECG}}_{I[N,M_N,p]}\middle|\hat{O}\middle|\phi^{\mathrm{apzFECG}}_{J[N,M_N,p]}\right\rangle\\ &= \left\langle\phi_I^{\mathrm{zFECG}}\middle|\hat{O}\middle|\hat{P}^{[N,p]}_{M_N}\phi_J^{\mathrm{zFECG}}\right\rangle,\end{aligned} \tag{29}$$

where the Hermiticity and idempotency of the projection operator, Eqs. (25) and (26), 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 $\hat{P}^{[p]}_{C_I}$ is omitted.

A. Overlap integral

The matrix elements of the identity operator for plain FECGs are given by [47]

$$\left\langle\phi_I^{\mathrm{FECG}}\middle|\phi_J^{\mathrm{FECG}}\right\rangle=\tilde{S}_{IJ}\,\exp\left[2\boldsymbol{s}_I^{(r)^T}A_I^{(r)}A_{IJ}^{(r)^{-1}}A_J^{(r)}\boldsymbol{s}_J^{(r)}\right], \tag{30}$$

where $A_{IJ}^{(r)}=A_I^{(r)}+A_J^{(r)}$ and

$$\begin{aligned}\tilde{S}_{IJ} = &\left(\frac{\pi^{N_p}}{\left|\bar{A}_I^{(r)}+\bar{A}_J^{(r)}\right|}\right)^{\frac{3}{2}}\exp\left[-\boldsymbol{s}_I^{(r)^T}A_I^{(r)}\boldsymbol{s}_I^{(r)}-\boldsymbol{s}_J^{(r)^T}A_J^{(r)}\boldsymbol{s}_J^{(r)}\right]\\ &\times\exp\left[+\boldsymbol{s}_I^{(r)^T}A_I^{(r)}A_{IJ}^{(r)^{-1}}A_I^{(r)}\boldsymbol{s}_I^{(r)}+\boldsymbol{s}_J^{(r)^T}A_J^{(r)}A_{IJ}^{(r)^T}A_J^{(r)}\boldsymbol{s}_J^{(r)}\right].\end{aligned} \tag{31}$$

In Eq. (30) we have separated $\tilde{S}_{IJ}$, the term unaffected by the action of the rotation operator on the shift vector $\boldsymbol{s}_J^{(r)}$. The remaining term must be investigated since it involves the angular integration over the Euler angles. For apzFECGs the

overlap matrix element reads

$$S^{\text{apzFECG}}_{IJ[N,M_N,p]} = \left\langle \phi_I^{\text{zFECG}}\left(\boldsymbol{r}; A_I^{(r)}, \boldsymbol{s}_I^{(r)}\right) \middle| \hat{P}^{[N,p]}_{M_N} \phi_J^{\text{zFECG}}\left(\boldsymbol{r}; A_J^{(r)}, \boldsymbol{s}_J^{(r)}\right) \right\rangle, \tag{32}$$

and writing explicitly the projection operator leads to

$$S^{\text{apzFECG}}_{IJ[N,M_N,p]} = \int \frac{d\Omega}{4\pi^3}\, D^{[N]}_{M_N M_N}(\Omega)^* \left\langle \phi_I\left(\boldsymbol{r}; A_I^{(r)}, \boldsymbol{s}_I^{(r)}\right) \middle| \phi_J\left(\boldsymbol{r}; A_J^{(r)}, U(\Omega)\boldsymbol{s}_J^{(r)}\right) \right\rangle, \tag{33}$$

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 $\hat{P}^{[N,p]}_{M_N}$, Eq. (33) can be written as

$$S^{\text{apzFECG}}_{IJ[N,M_N,p]} = \tilde{S}_{IJ}\, \Upsilon^N_{M_N}, \tag{34}$$

with

$$\Upsilon^N_{M_N} = \int \frac{d\Omega}{4\pi^3}\, D^{[N]}_{M_N M_N}(\Omega)^* \exp\left[2\, \boldsymbol{s}_I^{(r)^T} A_I^{(r)} A_{IJ}^{(r)^{-1}} A_J^{(r)} U(\Omega) \boldsymbol{s}_J^{(r)}\right]. \tag{35}$$

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

$$U(\Omega)\boldsymbol{s}_J^{(r)} = \boldsymbol{u}_J^{(r)} \otimes \tilde{U}(\Omega)\boldsymbol{e}_z, \tag{36}$$

where Eq. (27) and the definition of $U(\Omega)$ in Eq. (20) have been exploited.

Considering Eqs. (27), (36), and (28) and that $A_K^{(r)} = \bar{A}_K^{(r)} \otimes \mathbb{1}_3$ with $K \in \{I, J, IJ\}$, we have

$$\exp\left[2\, \boldsymbol{s}_I^{(r)^T} A_I^{(r)} A_{IJ}^{(r)^{-1}} A_J^{(r)} U(\Omega) \boldsymbol{s}_J^{(r)}\right] = \exp\left[C\, \boldsymbol{e}_z^T \tilde{U}(\Omega) \boldsymbol{e}_z\right] = \exp[C\, \cos\beta], \tag{37}$$

with C given as

$$C = 2\, \boldsymbol{u}_I^{(r)^T} \bar{A}_I^{(r)} \bar{A}_{IJ}^{(r)^{-1}} \bar{A}_J^{(r)} \boldsymbol{u}_J^{(r)}. \tag{38}$$

Finally, the angular integration reduces to

$$\Upsilon^N_{M_N} = \frac{1}{4\pi^3} \int_0^{2\pi} d\alpha \int_0^{\pi} d\beta \int_0^{2\pi} d\gamma\, \sin(\beta) D^{[N]^*}_{M_N M_N}(\Omega) \exp\left[C \cos(\beta)\right]. \tag{39}$$

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

$$D^{[N]}_{00}(\Omega) = D^{[N]}_{00}(\beta) = \sum_{\mu=0}^{N} a_\mu^{[N]} (\cos\beta)^\mu. \tag{40}$$

Therefore, for apzFECGs with $M_N = 0$, the integration over α and γ Euler angles is trivial and Eq. (39) becomes

$$\Upsilon^N_0 = \frac{1}{\pi} \sum_{\mu=0}^{N} \int_0^{\pi} d\beta \quad \sin(\beta)[\cos(\beta)]^\mu \exp\left[C \cos(\beta)\right]. \tag{41}$$

Furthermore, since apzFECG functions do not depend on Euler angles α and γ, the integration of the $D^{[N]^*}_{M_N M_N}(\Omega)$ yields zero for every $N \in \mathbb{N}_0$ and $M_N \neq 0$. The results of the integration over the Euler angle β in Eq. (41) for the spherically symmetric ground state as well as the two lowest rotationally excited states are then written as

$$\Upsilon^N_{M_N} = \begin{cases} \dfrac{2}{\pi C} \sinh(C), & N = 0\,,\ M_N = 0, \\ \dfrac{2}{\pi C} \cosh(C) - \dfrac{2}{\pi C^2} \sinh(C), & N = 1\,,\ M_N = 0, \\ \dfrac{2}{\pi C^3}\left[(C^2+3)\sinh(C) - 3C\cosh(C)\right], & N = 2\,,\ M_N = 0, \\ 0, & \forall N \in \mathbb{N}_0\,,\ M_N \neq 0. \end{cases} \tag{42}$$

For a list of $\Upsilon^N_{M_N}$ up to $N = 10$, see the Appendix.

B. Kinetic integral

The kinetic integral for plain FECGs reads [47]

$$\left\langle \phi_I^{\mathrm{FECG}} \right| - \nabla_{\boldsymbol{r}}^T M \nabla_{\boldsymbol{r}} \left| \phi_J^{\mathrm{FECG}} \right\rangle = \tilde{S}_{IJ} \left[4 \left(\boldsymbol{s}_I^{(r)} - \boldsymbol{s}_J^{(r)} \right)^T B \left(\boldsymbol{s}_I^{(r)} - \boldsymbol{s}_J^{(r)} \right) + 6 \,\mathrm{Tr}\left(M \bar{A}_J^{(r)} \bar{A}_{IJ}^{(r)^{-1}} \bar{A}_I^{(r)} \right) \right], \tag{43}$$

where

$$B = 4 A_J^{(r)} A_{IJ}^{(r)^{-1}} A_I^{(r)} M A_J^{(r)} A_{IJ}^{(r)^{-1}} A_I^{(r)}. \tag{44}$$

For apzFECGs it is

$$T_{IJ[N,M_N,p]}^{\mathrm{apzFECG}} = \left\langle \phi_I^{\mathrm{zFECG}} \right| \hat{P}_{M_N}^{[N,p]} \left| \phi_J^{\mathrm{zFECG}} \right\rangle = \tilde{S}_{IJ} \, \Sigma_{M_N}^N, \tag{45}$$

where the angular integral is written as

$$\Sigma_{M_N}^N = \int \frac{d\Omega}{4\pi^3} \, D_{M_N M_N}^{[N]}(\Omega)^* \exp[C \cos\beta] \left[-\boldsymbol{s}_I^{(r)^T} B \boldsymbol{s}_I^{(r)} - \boldsymbol{s}_J^{(r)^T} B \boldsymbol{s}_J^{(r)} + 2 \boldsymbol{s}_I^{(r)^T} B U(\Omega) \boldsymbol{s}_J^{(r)} + 6 \,\mathrm{Tr}\left(M \bar{A}_J^{(r)} \bar{A}_{IJ}^{(r)^{-1}} \bar{A}_I^{(r)} \right) \right]. \tag{46}$$

We define

$$\omega = -\boldsymbol{s}_I^{(r)^T} B \boldsymbol{s}_I^{(r)} - \boldsymbol{s}_J^{(r)^T} B \boldsymbol{s}_J^{(r)} + 6 \,\mathrm{Tr}\left(M \bar{A}_J^{(r)} \bar{A}_{IJ}^{(r)^{-1}} \bar{A}_I^{(r)} \right) \tag{47}$$

and

$$\sigma = 2 \boldsymbol{u}_I^{(r)\,T} \bar{B} \boldsymbol{u}_J^{(r)}, \tag{48}$$

so that Eq. (46) can be cast in the compact form

$$\Sigma_{M_N}^N = \int \frac{d\Omega}{4\pi^3} \, D_{M_N M_N}^{[N]}(\Omega)^* \, (\omega + \sigma \cos\beta) \, \exp[C \cos\beta]. \tag{49}$$

With Eq. (40), the integration over Euler angles can be reduced to the single integration over β for which these analytical results follow:

$$\Sigma_{M_N}^N = \begin{cases} \dfrac{2}{\pi C^2} [\sinh(C)(C\omega - \sigma) + C\sigma \cosh(C)], & N = 0,\ M_N = 0, \\ \dfrac{2}{\pi C^3} \{\sinh(C)\left[\left(C^2 + 2\right)\sigma - C\omega \right] + C \cosh(C)(C\omega - 2\sigma)\}, & N = 1,\ M_N = 0, \\ \dfrac{2}{\pi C^4} \{\sinh(C)[C(C^2 + 3)\omega - (4C^2 + 9)\sigma] \\ \qquad + C \cosh(C)[(C^2 + 9)\sigma - 3C\omega]\}, & N = 2,\ M_N = 0, \\ 0, & \forall N \in \mathbb{N}_0,\ M_N \neq 0. \end{cases} \tag{50}$$

For a list of $\Sigma_{M_N}^N$ up to $N = 10$, see the Appendix.

C. Coulomb integral

From Ref. [47] we retrieve the Coulomb matrix element for plain FECGs as follows:

$$\left\langle \phi_I^{\mathrm{FECG}} \left| \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \right| \phi_J^{\mathrm{FECG}} \right\rangle = \tilde{S}_{IJ} \left(\frac{1}{\boldsymbol{S}^T J_{ij} \boldsymbol{S}} \right)^{\frac{1}{2}} \mathrm{erf} \left[\left(\frac{\boldsymbol{S}^T J_{ij} \boldsymbol{S}}{\mathrm{Tr}\left(\bar{J}_{ij} \bar{A}_{IJ}^{(r)^{-1}} \right)} \right)^{\frac{1}{2}} \right], \tag{51}$$

where the vector $\boldsymbol{S}$ is defined as

$$\boldsymbol{S} = A_{IJ}^{(r)^{-1}} \left(A_I^{(r)} \boldsymbol{s}_I^{(r)} + A_J^{(r)} \boldsymbol{s}_J^{(r)} \right) \tag{52}$$

and

$$J_{ij} = \begin{cases} E_{ii} & \text{if } i = j, \\ E_{ii} + E_{jj} - E_{ij} - E_{ji} & \text{if } i \neq j, \end{cases} \tag{53}$$

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

$$V_{IJ[N,M_N,p]}^{\mathrm{apzFECG}} = \left\langle \phi_I^{\mathrm{zFECG}} \left| \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \right| \hat{P}_{M_N}^{[N,p]} \phi_J^{\mathrm{zFECG}} \right\rangle = \tilde{S}_{IJ} \, \Lambda_{M_N}^N, \tag{54}$$

where

$$\Lambda^N_{M_N} = \int \frac{d\Omega}{4\pi^3}\, D^{[N]}_{M_N M_N}(\Omega)^* e^{C\cos\beta}\left(\frac{1}{\tilde{\boldsymbol{S}}^T J_{ij}\tilde{\boldsymbol{S}}}\right)^{\frac{1}{2}} \mathrm{erf}\left[\left(\frac{\tilde{\boldsymbol{S}}^T J_{ij}\tilde{\boldsymbol{S}}}{\mathrm{Tr}\left(\bar{J}_{ij}\bar{A}^{(r)^{-1}}_{IJ}\right)}\right)^{\frac{1}{2}}\right]. \tag{55}$$

Here, we adopt the notation of Cafiero and Adamowicz [47] which is corrected in order to account for the rotated $\boldsymbol{s}_J$ vector

$$\tilde{\boldsymbol{S}} = A^{(r)^{-1}}_{IJ}\left(A^{(r)}_I \boldsymbol{s}^{(r)}_I + A^{(r)}_J U(\Omega)\boldsymbol{s}^{(r)}_J\right). \tag{56}$$

In order to make β explicit and solve the angular integration, we consider the following substitution:

$$\tilde{\boldsymbol{S}}^T J_{ij}\tilde{\boldsymbol{S}} = \tau_{ij} + 2\boldsymbol{s}^{(r)^T}_I A^{(r)}_I A^{(r)^{-1}}_{IJ} J_{ij} A^{(r)^{-1}}_{IJ} A^{(r)}_J U(\Omega)\boldsymbol{s}^{(r)}_J = \tau_{ij} + F_{ij}\left(\boldsymbol{e}^T_z \tilde{U}(\Omega)\boldsymbol{e}_z\right) = \tau_{ij} + F_{ij}\cos\beta, \tag{57}$$

with

$$\tau_{ij} = \boldsymbol{s}^{(r)^T}_I A^{(r)}_I A^{(r)^{-1}}_{IJ} J_{ij} A^{(r)^{-1}}_{IJ} A^{(r)}_I \boldsymbol{s}^{(r)}_I + \boldsymbol{s}^{(r)^T}_J A^{(r)}_J A^{(r)^{-1}}_{IJ} J_{ij} A^{(r)^{-1}}_{IJ} A^{(r)}_J \boldsymbol{s}^{(r)}_J, \tag{58}$$

$$F_{ij} = 2\boldsymbol{u}^{(r)^T}_I \bar{A}^{(r)}_I \bar{A}^{(r)^{-1}}_{IJ} \bar{J}_{ij} \bar{A}^{(r)^{-1}}_{IJ} \bar{A}^{(r)}_J \boldsymbol{u}^{(r)}_J. \tag{59}$$

The angular integration in Eq. (55) is now written as

$$\Lambda^N_{M_N} = \int \frac{d\Omega}{4\pi^3}\, D^{[N]}_{M_N M_N}(\Omega)^*\, e^{C\cos\beta}\left(\frac{1}{\tau_{ij} + F_{ij}\cos\beta}\right)^{\frac{1}{2}} \mathrm{erf}\left[\left(\frac{\tau_{ij} + F_{ij}\cos\beta}{\mathrm{Tr}\left(\bar{J}_{ij}\bar{A}^{(r)^{-1}}_{IJ}\right)}\right)^{\frac{1}{2}}\right]. \tag{60}$$

While the integration with respect to α and γ is trivial, to integrate over $\beta \in [0, \pi)$, we change the variable $y \equiv \tau_{ij} + F_{ij}\cos\beta$ so that Eq. (60) becomes

$$\Lambda^N_{M_N} = \frac{e^{-\frac{\tau_{ij}C}{F_{ij}}}}{\pi F_{ij}} \int_{\tau_{ij}-F_{ij}}^{\tau_{ij}+F_{ij}} dy\, D^{[N]}_{M_N M_N}(y)\, y^{-\frac{1}{2}}\, e^{\frac{C}{F_{ij}}y}\, \mathrm{erf}\left[\left(\frac{y}{\mathrm{Tr}\left(\bar{J}_{ij}\bar{A}^{(r)^{-1}}_{IJ}\right)}\right)^{\frac{1}{2}}\right]. \tag{61}$$

To change the variable of the Wigner D matrix we recall Eq. (40), namely, that the elements $D^{[N]}_{00}(\beta)$ for any N are polynomials of $\cos\beta$ of degree N. Therefore, after changing the variable, the zeroth diagonal element of the Wigner D matrix can be written as

$$D^{[N]}_{00}(y) = \sum_{\mu=0}^{N} a^{[N]}_\mu \left(\frac{y-\tau_{ij}}{F_{ij}}\right)^\mu = \sum_{\mu=0}^{N}\sum_{k=0}^{\mu} \frac{\mu!\, a^{[N]}_\mu}{(\mu-k)!k!}, \tag{62}$$

where in the second line the power of the binomial is written explicitly. By inserting Eq. (62), the polynomial form of the Wigner D matrix, Eq. (61) reads

$$\Lambda^N_0 = \frac{e^{-\frac{\tau_{ij}C}{F_{ij}}}}{\pi F_{ij}} \sum_{\mu=0}^{N}\sum_{k=0}^{\mu} \frac{\mu! a^{[N]}_\mu}{(\mu-k)!k!}\left(-\frac{\tau_{ij}}{F_{ij}}\right)^{\mu-k}\left(\frac{1}{F_{ij}}\right)^k \int_{\tau_{ij}-F_{ij}}^{\tau_{ij}+F_{ij}} dy\, y^{-\frac{1}{2}+k}\, e^{\frac{C}{F_{ij}}y}\, \mathrm{erf}\left[\left(\frac{y}{\mathrm{Tr}\left(\bar{J}_{ij}\bar{A}^{(r)^{-1}}_{IJ}\right)}\right)^{\frac{1}{2}}\right], \tag{63}$$

whereas expanding the exponential in a Taylor series yields

$$\Lambda^N_0 = \frac{e^{-\frac{\tau_{ij}C}{F_{ij}}}}{\pi F_{ij}} \sum_{\mu=0}^{N}\sum_{k=0}^{\mu} \frac{\mu! a^{[N]}_\mu}{(\mu-k)!k!}\left(-\frac{\tau_{ij}}{F_{ij}}\right)^{\mu-k}\left(\frac{1}{F_{ij}}\right)^k \sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{C}{F_{ij}}\right)^n \int_{\tau_{ij}-F_{ij}}^{\tau_{ij}+F_{ij}} dy\, y^{-\frac{1}{2}+k+n}\, \mathrm{erf}\left[\left(\frac{y}{\mathrm{Tr}\left(\bar{J}_{ij}\bar{A}^{(r)^{-1}}_{IJ}\right)}\right)^{\frac{1}{2}}\right]. \tag{64}$$

The integral over y possesses an analytical solution,

$$\begin{aligned}\Lambda^N_0 = {} & \frac{e^{-\frac{\tau_{ij}C}{F_{ij}}}}{\pi F_{ij}} \sum_{\mu=0}^{N}\sum_{k=0}^{\mu} \frac{\mu! a^{[N]}_\mu}{(\mu-k)!k!}\left(-\frac{\tau_{ij}}{F_{ij}}\right)^{\mu-k}\left(\frac{1}{F_{ij}}\right)^k \sum_{n=0}^{\infty}\frac{2}{(2k+2n+1)n!}\left(\frac{C}{F_{ij}}\right)^n \\ & \times\Bigg[-\mathrm{erf}\left(\sqrt{t_2}\right)(\tau_{ij}-F_{ij})^{k+n+\frac{1}{2}} + \mathrm{erf}\left(\sqrt{t_1}\right)(F_{ij}+\tau_{ij})^{k+n+\frac{1}{2}} \\ & + \frac{\mathrm{Tr}\left(\bar{J}_{ij}\bar{A}^{(r)^{-1}}_{IJ}\right)^{k+n+\frac{1}{2}}}{\sqrt{\pi}}\left(\Gamma(k+n+1,t_1) - \Gamma(k+n+1,t_2)\right)\Bigg],\end{aligned} \tag{65}$$

with

$$t_1 = \frac{\tau_{ij} + F_{ij}}{\mathrm{Tr}\left(\bar{J}_{ij}\bar{A}_{IJ}^{(r)^{-1}}\right)}, \tag{66}$$

$$t_2 = \frac{\tau_{ij} - F_{ij}}{\mathrm{Tr}\left(\bar{J}_{ij}\bar{A}_{IJ}^{(r)^{-1}}\right)}. \tag{67}$$

If the resulting series in Eq. (65) 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

$$\begin{aligned}\Lambda_0^N = \frac{e^{-\frac{\tau_{ij}C}{F_{ij}}}}{\pi F_{ij}} \sum_{\mu=0}^{N}\sum_{k=0}^{\mu} \frac{\mu! a_\mu^{[N]}}{(\mu-k)!k!}\left(-\frac{\tau_{ij}}{F_{ij}}\right)^{\mu-k}\left(\frac{1}{F_{ij}}\right)^k \Bigg[\left(-\frac{C}{F_{ij}}\right)^{-k-\frac{1}{2}} \mathrm{erf}\left(\sqrt{t_1}\right)\gamma\left(k+\frac{1}{2}, -\frac{C(F_{ij}+\tau_{ij})}{F_{ij}}\right) \\ - \left(-\frac{C}{F_{ij}}\right)^{-k-\frac{1}{2}} \mathrm{erf}\left(\sqrt{t_2}\right)\gamma\left(k+\frac{1}{2}, \frac{C(F_{ij}-\tau_{ij})}{F_{ij}}\right) + \frac{2}{\sqrt{\pi}}\sum_{n=0}^{\infty}\frac{\Gamma(k+n+1, t_1, t_2)}{n!(2k+2n+1)}\left(\frac{C}{F_{ij}}\right)^n \mathrm{Tr}\left(\bar{J}_{ij}\bar{A}_{IJ}^{(r)^{-1}}\right)^{k+n+\frac{1}{2}}\Bigg],\end{aligned} \tag{68}$$

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

$$\Gamma(n, t_1, t_2) = \Gamma(n)\left(e^{-t_1}\sum_{k=0}^{n-1}\frac{t_1^k}{k!} - e^{t_2}\sum_{k=0}^{n-1}\frac{t_2^k}{k!}\right). \tag{69}$$

While Eq. (68) 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. (63):

$$\Lambda_0^N = \frac{e^{-\frac{\tau_{ij}C}{F_{ij}}}}{\pi F_{ij}} \sum_{\mu=0}^{N}\sum_{k=0}^{\mu} \frac{\mu! a_\mu^{[N]}}{(\mu-k)!k!}\left(-\frac{\tau_{ij}}{F_{ij}}\right)^{\mu-k}\left(\frac{1}{F_{ij}}\right)^k 2T^{\frac{1}{2}}F_{ij}^k\frac{\partial^k}{\partial C^k}\int_{\sqrt{(\tau_{ij}-F_{ij})/T}}^{\sqrt{(\tau_{ij}+F_{ij})/T}} dx\, e^{\frac{CT}{F_{ij}}x^2}\,\mathrm{erf}\,[x], \tag{70}$$

where $T = \mathrm{Tr}(\bar{J}_{ij}\bar{A}_{IJ}^{(r)^{-1}})$, the integration variable is changed according to $(y/T)^{\frac{1}{2}} = x$, and the kth derivative with respect to C is considered. The integral in Eq. (70) possesses an analytical solution,

$$\int_a^b dx\, e^{-qx^2}\,\mathrm{erf}\,[x] = 2\sqrt{\frac{\pi}{q}}\left[T\left(a\sqrt{2q}, \frac{1}{\sqrt{q}}\right) - T\left(b\sqrt{2q}, \frac{1}{\sqrt{q}}\right)\right], \tag{71}$$

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

D. Squared total angular momentum expectation value

To solve $\langle\phi_I^{\mathrm{zFECG}}|\hat{N}^2|\phi_J^{\mathrm{apzFECG}}\rangle$, the squared total angular momentum expectation value for projected zFECG functions, we start from the matrix elements for FECGs derived in our previous work [40]:

$$\left\langle\phi_I^{\mathrm{FECG}}\middle|\hat{N}^2\middle|\phi_J^{\mathrm{FECG}}\right\rangle = \epsilon'_{ijk}\left[2\left(\boldsymbol{s}_I^{(r)^T}\omega_I^{(j,k)^T}A_{IJ}^{(r)^{-1}}\omega_J^{(j,k)}\boldsymbol{s}_J^{(r)}\right) + 4\left(\boldsymbol{w}^T A_{IJ}^{(r)^{-1}}\omega_J^{(j,k)}\boldsymbol{s}_J^{(r)}\right)\left(\boldsymbol{w}^T A_{IJ}^{(r)^{-1}}\omega_I^{(j,k)}\boldsymbol{s}_I^{(r)}\right)\right]S_{IJ}^{\mathrm{FECG}}, \tag{72}$$

where $\boldsymbol{w} = A_I^{(r)}\boldsymbol{s}_I^{(r)} + A_J^{(r)}\boldsymbol{s}_J^{(r)}$, ϵ'_{ijk} is the Levi-Civita symbol for which only the negative entries are set to zero, and

$$\omega_K^{(x,y)} = \bar{A}_K^{(r)} \otimes \left(E_{xy} - E_{yx}\right), \quad \text{with } K \in \{I, J\}, \tag{73}$$

with $(E_{ij})_{xy} = \delta_{ix}\delta_{jy}$. Note that the i, j, and k indices are summed with Einstein's summation convention. We recall that for apzFECG functions, the vector $\boldsymbol{s}_K^{(r)}$ ($K \in \{I, J\}$) must obey the constraint introduced in Eq. (27) and $\boldsymbol{s}_J^{(r)}$ is subject to the rotation operator $\hat{R}(\Omega)$ involving the transformation matrix $U(\Omega)$. Considering Eqs. (27), (36), (28), and (73) we have

$$\left\langle\phi_I^{\mathrm{zFECG}}\middle|\hat{N}^2\middle|\phi_{J[N,M_N,p]}^{\mathrm{apzFECG}}\right\rangle = \tilde{S}_{IJ}\ \Xi_{M_N}^N, \tag{74}$$

where

$$\begin{aligned}\Xi_{M_N}^N = \epsilon'_{ijk}\int\frac{d\Omega}{4\pi^3}\, D_{M_N M_N}^{[N]}(\Omega)^*\, e^{C\cos\beta}\Big(2\left(\boldsymbol{u}_I^{(r)^T}\bar{A}_I^{(r)}\bar{A}_{IJ}^{(r)^{-1}}\bar{A}_J^{(r)}\boldsymbol{u}_J^{(r)}\right)\left[\boldsymbol{e}_z^T(E_{jk}-E_{kj})^T(E_{jk}-E_{kj})\tilde{U}(\Omega)\boldsymbol{e}_z\right] \\ + 4\Big\{\left(\boldsymbol{u}_I^{(r)^T}\bar{A}_I^{(r)}\bar{A}_{IJ}^{(r)^{-1}}\bar{A}_J^{(r)}\boldsymbol{u}_J^{(r)}\right)\left[\boldsymbol{e}_z^T(E_{jk}-E_{kj})\tilde{U}(\Omega)\boldsymbol{e}_z\right] + \left(\boldsymbol{u}_J^{(r)^T}\bar{A}_J^{(r)}\bar{A}_{IJ}^{(r)^{-1}}\bar{A}_J^{(r)}\boldsymbol{u}_J^{(r)}\right)\left[\boldsymbol{e}_z^T\tilde{U}(\Omega)^T(E_{jk}-E_{kj})\tilde{U}(\Omega)\boldsymbol{e}_z\right]\Big\} \\ \times\Big\{\left(\boldsymbol{u}_I^{(r)^T}\bar{A}_I^{(r)}\bar{A}_{IJ}^{(r)^{-1}}\bar{A}_I^{(r)}\boldsymbol{u}_I^{(r)}\right)\left[\boldsymbol{e}_z^T(E_{jk}-E_{kj})\boldsymbol{e}_z\right] + \left(\boldsymbol{u}_J^{(r)^T}\bar{A}_J^{(r)}\bar{A}_{IJ}^{(r)^{-1}}\bar{A}_I^{(r)}\boldsymbol{u}_I^{(r)}\right)\left[\boldsymbol{e}_z^T\tilde{U}(\Omega)^T(E_{jk}-E_{kj})\boldsymbol{e}_z\right]\Big\}\Big),\end{aligned} \tag{75}$$

where C has been defined in Eq. (38).

Furthermore, provided that $(j,k) \in \{(2,3),(3,1),(1,2)\}$ (see Ref. [40] for a detailed demonstration), we have

$$\boldsymbol{e}_z^T (E_{23}-E_{32})^T (E_{23}-E_{32})\tilde{U}(\Omega)\boldsymbol{e}_z = \cos\beta, \tag{76}$$

$$\boldsymbol{e}_z^T (E_{31}-E_{13})^T (E_{31}-E_{13})\tilde{U}(\Omega)\boldsymbol{e}_z = \cos\beta, \tag{77}$$

$$\boldsymbol{e}_z^T (E_{23}-E_{32})\tilde{U}(\Omega)\boldsymbol{e}_z = +\sin\alpha\ \sin\beta, \tag{78}$$

$$\boldsymbol{e}_z^T (E_{31}-E_{13})\tilde{U}(\Omega)\boldsymbol{e}_z = -\cos\alpha\ \sin\beta, \tag{79}$$

$$\boldsymbol{e}_z^T \tilde{U}(\Omega)^T (E_{23}-E_{32})\tilde{U}(\Omega)\boldsymbol{e}_z = 0, \tag{80}$$

$$\boldsymbol{e}_z^T \tilde{U}(\Omega)^T (E_{31}-E_{13})\tilde{U}(\Omega)\boldsymbol{e}_z = 0, \tag{81}$$

$$\boldsymbol{e}_z^T (E_{23}-E_{32})\boldsymbol{e}_z = 0, \tag{82}$$

$$\boldsymbol{e}_z^T (E_{31}-E_{13})\boldsymbol{e}_z = 0, \tag{83}$$

$$\boldsymbol{e}_z^T \tilde{U}(\Omega)^T (E_{23}-E_{32})\boldsymbol{e}_z = -\sin\alpha\sin\beta, \tag{84}$$

$$\boldsymbol{e}_z^T \tilde{U}(\Omega)^T (E_{31}-E_{13})\boldsymbol{e}_z = +\cos\alpha\sin\beta, \tag{85}$$

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

Equation (75) can now be written as

$$\Xi^N_{M_N} = \int \frac{d\Omega}{4\pi^3} D^{[N]}_{M_N M_N}(\Omega)^* \exp[C\cos\beta] \times [2(C\cos\beta) + (C\sin\alpha\ \sin\beta)(-C\sin\alpha\sin\beta) + (-C\cos\alpha\sin\beta)(C\cos\alpha\sin\beta)], \tag{86}$$

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

$$\Xi^N_{M_N} = \begin{cases} 0 & \text{if} \quad N=0,\ M_N=0, \\ 2\Upsilon^1_0 & \text{if} \quad N=1,\ M_N=0, \\ 6\Upsilon^2_0 & \text{if} \quad N=2,\ M_N=0, \\ 0 & \forall N \in \mathbb{N}_0,\ M_N \neq 0, \end{cases} \tag{87}$$

where $\Upsilon^N_{M_N}$ are the solutions of the overlap angular integration given in Eq. (42). This is in accordance with the expected eigenvalue for the squared total spatial angular momentum $N(N+1)$ in Hartree atomic units. For a list of $\Xi^N_{M_N}$ up to $N = 5$, see the Appendix.

E. Projection of the angular momentum onto the z axis

We recall the $\langle \hat{N}_z \rangle_{IJ}$ matrix elements for FECG functions [40]

$$\left\langle \phi_I^{\text{FECG}} \middle| \hat{N}_z \middle| \phi_J^{\text{FECG}} \right\rangle = \frac{2}{i}\left(\boldsymbol{w}^T A_{IJ}^{(r)^{-1}} \omega_J^{(1,2)} \boldsymbol{s}_J^{(r)}\right) \langle \phi_I | \phi_j \rangle. \tag{88}$$

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

$$\begin{aligned} \boldsymbol{w}^T A_{IJ}^{(r)^{-1}} \omega_J^{(1,2)} \boldsymbol{s}_J^{(r)} &= \boldsymbol{s}_I^{(r)^T} A_I^{(r)} A_{IJ}^{(r)^{-1}} \omega_J^{(1,2)} \boldsymbol{s}_J^{(r)} + \boldsymbol{s}_J^{(r)^T} A_J^{(r)} A_{IJ}^{(r)^{-1}} \omega_J^{(1,2)} \boldsymbol{s}_J^{(r)} \\ &= \left(\boldsymbol{u}_I^{(r)^T} \bar{A}_I^{(r)} \bar{A}_{IJ}^{(r)^{-1}} \bar{A}_J^{(r)} \boldsymbol{u}_J^{(r)}\right)\left(\boldsymbol{e}_z^T \tilde{U}(\Omega')(E_{21}-E_{12})\tilde{U}(\Omega)\boldsymbol{e}_z\right) \\ &\quad + \left(\boldsymbol{u}_J^{(r)^T} \bar{A}_J^{(r)} \bar{A}_{IJ}^{(r)^{-1}} \bar{A}_J^{(r)} \boldsymbol{u}_J^{(r)}\right)\left(\boldsymbol{e}_z^T \tilde{U}(\Omega)^T (E_{21}-E_{12})\tilde{U}(\Omega)\boldsymbol{e}_z\right) = 0. \end{aligned} \tag{89}$$

It follows from Eqs. (80) and (81) that the latter term is zero, i.e., $\boldsymbol{e}_z^T \tilde{U}(\Omega)(E_{21}-E_{12})\tilde{U}(\Omega)\boldsymbol{e}_z = 0$, while the former one is

$$\boldsymbol{e}_z^T \tilde{U}(\Omega')(E_{21}-E_{12})\tilde{U}(\Omega)\boldsymbol{e}_z = \cos\alpha' \sin\alpha \sin\beta \sin\beta' - \cos\alpha \sin\alpha' \sin\beta \sin\beta'. \tag{90}$$

The resulting expectation value for apzFECG functions reads

$$\begin{aligned} \left\langle \phi^{\text{apzFECG}}_{I[N,M_N,p]} \middle| \hat{N}_z \middle| \phi^{\text{apzFECG}}_{J[N,M_N,p]} \right\rangle &= \tilde{S}_{IJ} \int \frac{d\Omega}{4\pi^3} \int \frac{d\Omega'}{4\pi^3} D^{[N]}_{M_N M_N}(\Omega)^* D^{[N]}_{M_N M_N}(\Omega')^* \exp[C\ \cos\beta] \\ &\quad \times \left(\boldsymbol{u}_I^{(r)^T} \bar{A}_I^{(r)} \bar{A}_{IJ}^{(r)^{-1}} \bar{A}_J^{(r)} \boldsymbol{u}_J^{(r)}\right)[\sin(\alpha-\alpha')(\sin\beta)^2(\sin\beta')^2], \end{aligned} \tag{91}$$

which evaluates to zero for every N, M_N pair:

$$\left\langle \phi^{\text{apzFECG}}_{I[N,M_N,p]} \middle| \hat{N}_z \middle| \phi^{\text{apzFECG}}_{J[N,M_N,p]} \right\rangle = 0 \quad \forall\ N \mid N = (0,1,2,\ldots), \quad M_N = (-N,\ldots,+N). \tag{92}$$

This shows that apzFECG functions have zero projection of the total angular momentum on the z axis. The results in this section can be expanded by noting that not only the expectation value of $\hat{N}_z$ is zero but also the corresponding eigenvalue of the apzFECG functions,

$$\hat{N}_z \phi^{\text{apzFECG}}_{I[N,M_N,p]} = 0. \tag{93}$$

The derivation of Eq. (93) follows from the definition of $\phi^{\text{apzFECG}}_{I[N,M_N,p]}$, $\hat{N}_z$, and $P^{[N,p]}_{M_N}$:

$$\begin{aligned} \hat{N}_z \phi^{\text{apzFECG}}_{I[N,M_N,p]} &= \hat{N}_z P^{[N,p]}_{M_N} \phi_I^{\text{zFECG}}\left(\boldsymbol{r}; A_I^{(r)}, \boldsymbol{s}_I^{(r)}\right) = \hat{N}_z \int \frac{d\Omega}{4\pi^3} D^{[N]}_{M_N M_N}(\Omega)^* \phi_I^{\text{zFECG}}\left(\boldsymbol{r}; A_I^{(r)}, U(\Omega)\boldsymbol{s}_I^{(r)}\right) \\ &= \frac{2}{i} \int \frac{d\Omega}{4\pi^3} D^{[N]}_{M_N M_N}(\Omega)^* \left[\boldsymbol{r}^T \omega_I^{(x,y)} U(\Omega)\boldsymbol{s}_I^{(r)}\right] \phi_I^{\text{zFECG}}\left(\boldsymbol{r}; A_I^{(r)}, U(\Omega)\boldsymbol{s}_I^{(r)}\right), \end{aligned} \tag{94}$$

and by noting that

$$U(\Omega)\boldsymbol{s}_I^{(r)} = \boldsymbol{u}_I^{(r)} \otimes \tilde{U}(\Omega)\boldsymbol{e}_z = \boldsymbol{u}_I^{(r)} \otimes \begin{pmatrix} -\cos\alpha\sin\beta \\ -\sin\alpha\sin\beta\cos\beta \\ \cos\beta \end{pmatrix}. \tag{95}$$

Since $D^{[N]}_{M_N M_N} \propto \exp(-iM_N\gamma)$ and the right-hand side of Eq. (94) do not depend on γ, the integration over the Euler angles yields zero for all $M_N \neq 0$. This shows that Eq. (93) is correct, and additionally, we have

$$\phi^{\text{apzFECG}}_{I\,[N,M_N,p]} = \hat{P}^{[N,p]}_{M_N}\phi_I^{\text{zFECG}} = 0 \quad \forall M_N \neq 0, \tag{96}$$

i.e., there is no component of ϕ_I^{zFECG} on the $M_N \neq 0$ eigenspaces.

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 Refs. [42,43]. First, the variational matrices $A^{(r)}$ and the variational vectors $\boldsymbol{s}^{(r)}$ are manipulated in a given TICC, $A^{(x)}$ and $\boldsymbol{s}^{(x)}$, respectively, and defined in block diagonal form:

$$\bar{A}_I^{(r)} = U_x^T \begin{pmatrix} \mathcal{A}_I^{(x)} & 0 \\ 0 & c_A \end{pmatrix} U_x, \tag{97}$$

$$\boldsymbol{s}_I^{(r)} = U_x \begin{pmatrix} \boldsymbol{s}_I^{(x)} \\ \boldsymbol{c}_S \end{pmatrix} = U_x \begin{pmatrix} \boldsymbol{u}_I^{(x)} \\ c_{S_z} \end{pmatrix} \otimes \boldsymbol{e}_z, \tag{98}$$

where the $N_p - 1 \times N_p - 1$ matrix $\mathcal{A}_I^{(x)}$ and the $N_p - 1$ vector $\boldsymbol{u}_I^{(x)}$ are related to the internal coordinates, while c_A and c_{S_z} are scalar parameters associated with 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_A and c_{S_z} for all $I \in \{1,\ldots,N_b\}$ would systematically cancel center-of-mass contributions from every expectation value, $c_A = 0$ leads to a singular matrix A_I, which violates the square-integrable and positive-definiteness requirements for the basis functions.

We note that the choice of $c_A = 1$ and $c_{S_z} = 0$ implies that every FECG, zFECG, or apzFECG function is exactly factorizable into a spherical Gaussian centered at the origin for the center-of-mass coordinate, and an FECG function for the $N_p - 1$ internal coordinates. In fact, the FECG in (transformed) TICC coordinates $\{x\}$ can be written as

$$\begin{aligned}\phi_I^{\text{FECG}} &= \exp\left[-\begin{pmatrix} \boldsymbol{x} - \boldsymbol{s}_I^{(x)} \\ \boldsymbol{x}_{\text{CM}} - \boldsymbol{c}_S \end{pmatrix}^T \begin{pmatrix} \mathcal{A}_I^{(x)} & 0 \\ 0 & c_A \end{pmatrix} \begin{pmatrix} \boldsymbol{x} - \boldsymbol{s}_I^{(x)} \\ \boldsymbol{x}_{\text{CM}} - \boldsymbol{c}_S \end{pmatrix}\right] \\ &= \exp\left[-\left(\boldsymbol{x} - \boldsymbol{s}_I^{(x)}\right)^T \mathcal{A}_I^{(x)}\left(\boldsymbol{x} - \boldsymbol{s}_I^{(x)}\right)\right] \exp\left[-\boldsymbol{x}_{\text{CM}}^2\right].\end{aligned} \tag{99}$$

We choose not to evaluate the integral matrix elements with basis functions and operators in a (transformed) TICC set. Instead, we carry out the integrations straightforwardly in the simple LFCC set and correct *a posteriori* the resulting expression by subtracting center-of-mass-dependent terms as described in our previous work. Hence, elimination of center-of-mass contaminations is equivalent to subtraction of the residual c_A terms [42,43].

We start detecting c_A-dependent terms from the C factor. To this aim, we transform it to the TICC sets $\{x\}$ and $\{y\}$, for the Ith and Jth basis functions, respectively,

$$\begin{aligned} C &= 2\boldsymbol{u}_I^{(r)T}\bar{A}_I^{(r)}\bar{A}_{IJ}^{(r)^{-1}}\bar{A}_J^{(r)}\boldsymbol{u}_J^{(r)} \\ &= 2\boldsymbol{u}_I^{(r)T}\left[U_x^T\bar{A}_I^{(x)}U_x\bar{A}_{IJ}^{(r)^{-1}}U_y^T\bar{A}_I^{(y)}U_y\right]\boldsymbol{u}_J^{(r)} \\ &= 2\boldsymbol{u}_I^{(r)T}\left[U_x^T\begin{pmatrix}\mathcal{A}_I^{(x)} & 0\\ 0 & c_A\end{pmatrix}\begin{pmatrix}\mathcal{A}_{IJ}^{-1} & 0\\ 0 & \frac{1}{2c_A}\end{pmatrix}\begin{pmatrix}\mathcal{A}_J^{(y)} & 0\\ 0 & c_A\end{pmatrix}U_x\right]\boldsymbol{u}_J^{(r)} \\ &= 2\begin{pmatrix}\boldsymbol{u}_I^{(x)}c_{S_z}\end{pmatrix}\begin{pmatrix}\mathcal{A}_I^{(x)}\mathcal{A}_{IJ}^{-1}\mathcal{A}_J^{(y)} & 0\\ 0 & \frac{c_A}{2}\end{pmatrix}\begin{pmatrix}\boldsymbol{u}_J^{(y)}\\ c_{S_z}\end{pmatrix}, \end{aligned} \tag{100}$$

where $\mathcal{A}_{IJ} = \mathcal{A}_I + \mathcal{A}_J$. In the third step, the following mathematical relation is employed [43]:

$$U_x\bar{A}_{IJ}^{-1}U_y^T = \begin{pmatrix}\mathcal{A}_{IJ}^{-1} & 0\\ 0 & \frac{1}{2c_A}\end{pmatrix}. \tag{101}$$

From Eq. (100) it follows that the center-of-mass contributions to C are zero for $c_{S_z} = 0$. For this reason, since the expectation value of the total angular momentum squared operator depends solely on C terms, we conclude that it is free of center-of-mass contaminations.

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

$$R = \text{Tr}\left(MA_J^{(r)}A_{IJ}^{(r)^{-1}}A_I^{(r)}\right). \tag{102}$$

The translational contamination can now be eliminated by replacing

$$R_{\text{corr.}} = R - \tfrac{1}{4}c_Ac_M, \tag{103}$$

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 $N_p - 1$ pseudoparticles 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

$$\Phi^{\text{apzFECG}}_{I\,[N,M_N,p]} = \frac{\hat{P}^{[N,p]}_{M_N}\phi_I^{\text{zFECG}}}{\left|\phi^{\text{apzFECG}}_{I\,[N,M_N,p]}\right|}, \tag{104}$$

where the normalization factor is

$$\left|\phi_I^{[N,M_N]}\right| = \left\langle \hat{P}^{[N,p]}_{M_N}\phi^{\text{apzFECG}}_{I[N,M_N,p]} \middle| \hat{P}^{[N,p]}_{M_N}\phi^{\text{apzFECG}}_{I[N,M_N,p]}\right\rangle^{\frac{1}{2}}. \tag{105}$$

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

$$\begin{aligned}&\left\langle \Phi^{\text{apzFECG}}_{I[N,M_N,p]}\middle|\hat{O}\middle|\Phi^{\text{apzFECG}}_{J[N,M_N,p]}\right\rangle \\ &\quad= \frac{\left\langle \hat{P}^{[N,p]}_{M_N}\phi^{\text{zFECG}}_{I[N,M_N,p]}\middle|\hat{O}\middle|\hat{P}^{[N,p]}_{M_N}\phi^{\text{zFECG}}_{J[N,M_N,p]}\right\rangle}{\left|\phi^{\text{apzFECG}}_{I[N,M_N,p]}\right|\left|\phi^{\text{apzFECG}}_{J[N,M_N,p]}\right|}.\end{aligned} \tag{106}$$

TABLE I. Nonrelativistic energies of $H_2{}^+ = \{p^+, p^+, e^-\}$, compared with results from Ref. [53] in the last column. The calculations include all possible Jacobi coordinates, the heavy-particle-centered, and the center-of-mass-centered coordinate sets. Here, $\Delta E = E(\text{Ref. [53]}) - \langle\hat{H}\rangle$.

	$\langle\hat{H}\rangle/E_\text{h}$ ($N_b = 400$)	η	$\langle\hat{H}\rangle_\text{Ref.}/E_\text{h}$ ($N_b = 4000$)	$\Delta E/nE_\text{h}$
$N = 0$	−0.597 139 062 111	10^{-9}	−0.597 139 063 079	−0.968
$N = 1$	−0.596 873 736 772	10^{-9}	−0.596 873 738 784	−2.012
$N = 2$	−0.596 345 204 133	10^{-9}	−0.596 345 205 489	−1.356

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.

The accuracy and convergence of special functions, i.e., the hyperbolic sine and cosine functions and the generalized incomplete Gamma functions, converge to $0.9\,\varepsilon$ for every point without the need to resort to higher-precision arithmetics. The latter we implemented for the handling of particularly difficult cases following Refs. [48,49].

Comparing apzFECGs for $N = 0$ and the spherically symmetric (simple) ECG functions, we note that the former require systematically less function evaluations to reach a given accuracy. Simple ECG functions are plagued by problems of linear dependence in the basis during energy optimization of a polyatomic system. In diatomics, there exists a large nuclear density at a distance to the origin in relative coordinates. Simple ECG functions account for this by requiring nearly overlapping terms in the linear combinations with large matching linear coefficients of opposite sign. This near-linear dependency in the basis complicates optimization and yields numerically unstable eigensystems with ill-conditioned Hamiltonian matrices. Conversely, we did not encounter such severe near-linear dependencies with apzFECG functions because these functions can effectively separate the proton densities along an axis.

VI. NUMERICAL RESULTS

The formulas derived we 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 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 set 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 [41], 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 [41] 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 nonlinear variational parameters was crucial to achieve efficient energy convergence. This optimization problem of minimizing the energy with respect to the set of nonlinear parameters is a difficult problem as the objective function is nonconvex, nonseparable, and often (Sec. V G) ill conditioned. We relied on two derivative-free algorithms: the subplex algorithm by Rowan [50] and the principal axis method discussed by Brent [51]. In our computer implementation of both methods, we used the NLOPT package [52]. We employed our multichannel optimization approach presented in our previous work [43], and we have included every possible set of Jacobi coordinates, the heavy-particle-centered coordinates, and the center-of-mass-centered coordinates. The construction of the Gaussian parameters through different U_a^TICC maps allows us to explore

TABLE II. Nonrelativistic energies of $H_2 = \{p^+, p^+, e^-, e^-\}$, compared with results from Ref. [54] in the last column. The calculations include all possible Jacobi coordinates, the heavy-particle-centered, and the center-of-mass-centered coordinate sets. Here, $\Delta E = E(\text{Ref. [54]}) - \langle\hat{H}\rangle$.

	$\langle\hat{H}\rangle/E_\text{h}$ ($N_b = 600$)	η	$\langle\hat{H}\rangle_\text{Ref.}/E_\text{h}$ ($N_b = 4200$)	$\Delta E/nE_\text{h}$
$N = 0$	−1.164 025 024 82	10^{-8}	−1.164 025 031	−6.18
$N = 1$	−1.163 485 167 09	10^{-8}	−1.163 485 173	−5.91
$N = 2$	−1.162 410 405 66	10^{-7}	−1.162 410 409	−3.34

the parameter space faster and to describe different groupings of the particles with the most appropriate TICC set. These calculations were carried out using message passing interface parallelization on six multiprocessor computer platforms (e.g., the AMD Opteron Processor 6376).

We compare the results for $H_2{}^+$ and H_2 with Refs. [53,54], respectively. Earlier results obtained with unprojected FECG and numerically projected FECG functions (with three-dimensional shifted centers) for H_2 with a basis set size of $N_b = 1560$ are 1.162 739 and 1.163 998 E_h, respectively [40]. The wall time of these earlier calculations was about three months. Our best result with only 600 linearly combined apzFECGs for the rotational ground state of H_2 is $-1.164\,025\,024\,82$ E_h. Accordingly, the wall time of the calculation was reduced to about two months, yielding a result of higher accuracy. Investigating the results in Tables I and II, we observe that the energies are well converged with the number of basis functions. The optimized basis-function parameters are deposited in the Supplemental Material [55].

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 Gaussian functions 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 resulting analytically projected zFECGs can potentially target any rotational state. This can be done efficiently because they are eigenfunctions of the total (nuclei plus electrons) squared spatial angular momentum operator $\hat{N}^2$ with eigenvalue N and of $\hat{N}_z$ with eigenvalue $M_N = 0$. Since only states with zero total spatial angular momentum projection onto the z axis can be accessed, among the $2N + 1$ degenerate states with $M_N = -N, \ldots, +N$, these functions are not suited in applications for which these degeneracies are lifted, e.g., in the presence of external magnetic fields. Despite this limitation, projected zFECGs address the problem of targeting rotationally excited states exactly, whereas other explicitly correlated basis functions either specialize on one specific N considering only lowest-order angular momentum couplings for the ease of the Hamiltonian matrix elements, or resemble the correct partial wave decomposition only for very high linear combinations and in the variational limit with the so-called global vector representation. The numerical examples presented demonstrate the correctness of the derived formulas and the applicability of the approach to excited rotational states of small molecules.

Particularly interesting will be the application of our analytical projection method to shift vectors lying on a plane and the extension to floating Gaussian functions with preexponential factors which can well represent the radial nodes of, for example, pure vibrational states. Such calculations are beyond the scope of the present paper and are therefore deferred to future work.

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APPENDIX: LIST OF INTEGRALS

This Appendix reviews the solutions to the principal integrals of the overlap, kinetic, and total angular momentum squared integral matrix elements for apzFECG functions. All formulas have been checked for consistency against multiple implementations and known special cases ($\boldsymbol{s}_I = 0$, $C = 0$). The list of analytical solution to the principal integrals for $N \in [0, 10]$ is as follows:

$$\Upsilon_0^0 = \frac{2}{\pi C}\sinh(C), \tag{A1}$$

$$\Upsilon_0^1 = \frac{2}{\pi C}\cosh(C) - \frac{2}{\pi C^2}\sinh(C), \tag{A2}$$

$$\Upsilon_0^2 = \frac{2}{\pi C^3}[(C^2+3)\sinh(C) - 3C\cosh(C)], \tag{A3}$$

$$\Upsilon_0^3 = \frac{2}{\pi C^4}[C(C^2+15)\cosh(C) - 3(2C^2+5)\sinh(C)], \tag{A4}$$

$$\Upsilon_0^4 = \frac{2}{\pi C^5}[(C^4+45C^2+105)\sinh(C) - 5C(2C^2+21)\cosh(C)], \tag{A5}$$

$$\Upsilon_0^5 = \frac{2}{\pi C^6}[C(C^4+105C^2+945)\cosh(C) - 15(C^4+28C^2+63)\sinh(C)], \tag{A6}$$

$$\Upsilon_0^6 = \frac{2}{\pi C^7}[(C^6+210C^4+4725C^2+10395)\sinh(C) - 21C(C^4+60C^2+495)\cosh(C)], \tag{A7}$$

$$\Upsilon_0^7 = \frac{2}{\pi C^8}[C(C^6+378C^4+17325C^2+135135)\cosh(C) - 7(4C^6+450C^4+8910C^2+19305)\sinh(C)], \tag{A8}$$

$$\Upsilon_0^8 = \frac{2}{\pi C^9}[(C^8+630C^6+51975C^4+945945C^2+2027025)\sinh(C) - 9C(4C^6+770C^4+30030C^2+225225)\cosh(C)], \tag{A9}$$

$$\Upsilon_0^9 = \frac{2}{\pi C^{10}}[C(C^8+990C^6+135135C^4+4729725C^2+34459425)\cosh(C) - 45(C^8+308C^6+21021C^4+360360C^2+765765)\sinh(C)], \tag{A10}$$

$$\Upsilon_0^{10} = \frac{2}{\pi C^{11}}[(C^{10} + 1485C^8 + 315315C^6 + 18918900C^4 + 310134825C^2 + 654729075)\sinh(C) - 55C(C^8 + 468C^6 + 51597C^4 + 1670760C^2 + 11904165)\cosh(C)], \tag{A11}$$

$$\Sigma_0^0 = \frac{2}{\pi C^2}[\sinh(C)(C\omega - \sigma) + C\sigma\cosh(C)], \tag{A12}$$

$$\Sigma_0^1 = \frac{2}{\pi C^3}\{\sinh(C)[(C^2 + 2)\sigma - C\omega] + C\cosh(C)(C\omega - 2\sigma)\}, \tag{A13}$$

$$\Sigma_0^2 = \frac{2}{\pi C^4}\{\sinh(C)[C(C^2 + 3)\omega - (4C^2 + 9)\sigma]\}, \tag{A14}$$

$$\Sigma_0^3 = \frac{2}{\pi C^5}\{C\cosh(C)[C(C^2 + 15)\omega - (7C^2 + 60)\sigma] + \sinh(C)[(C^4 + 27C^2 + 60)\sigma - 3C(2C^2 + 5)\omega]\}, \tag{A15}$$

$$\Sigma_0^4 = \frac{2}{\pi C^6}\{\sinh(C)[C(C^4 + 45C^2 + 105)\omega - (11C^4 + 240C^2 + 525)\sigma] + C\cosh(C)[(C^4 + 65C^2 + 525)\sigma - 5C(2C^2 + 21)\omega]\}, \tag{A16}$$

$$\Sigma_0^5 = \frac{2}{\pi C^7}\{C\cosh(C)[C(C^4 + 105C^2 + 945)\omega - (16C^4 + 735C^2 + 5670)\sigma] + \sinh(C)[(C^6 + 135C^4 + 2625C^2 + 5670)\sigma - 15C(C^4 + 28C^2 + 63)\omega]\}, \tag{A17}$$

$$\Sigma_0^6 = \frac{2}{\pi C^8}\{\sinh(C)[C(C^6 + 210C^4 + 4725C^2 + 10395)\omega - (22C^6 + 1890C^4 + 34020C^2 + 72765)\sigma] + C\cosh(C)[(C^6 + 252C^4 + 9765C^2 + 72765)\sigma - 21C(C^4 + 60C^2 + 495)\omega]\}, \tag{A18}$$

$$\Sigma_0^7 = \frac{2}{\pi C^9}\{\cosh(C)[C(C^6 + 378C^4 + 17325C^2 + 135135)\omega - (29C^6 + 4284C^4 + 148995C^2 + 1081080)\sigma] + \sinh(C)[(C^8 + 434C^6 + 29925C^4 + 509355C^2 + 1081080)\sigma - 7C(4C^6 + 450C^4 + 8910C^2 + 19305)\omega]\}, \tag{A19}$$

$$\Sigma_0^8 = \frac{2}{\pi C^{10}}\{\sinh(C)[C(C^8 + 630C^6 + 51975C^4 + 945945C^2 + 2027025)\omega - (37C^8 + 8820C^6 + 530145C^4 + 8648640C^2 + 18243225)\sigma] + C\cosh(C)[(C^8 + 702C^6 + 79695C^4 + 2567565C^2 + 18243225)\sigma - 9C(4C^6 + 770C^4 + 30030C^2 + 225225)\omega]\}, \tag{A20}$$

$$\Sigma_0^9 = \frac{2}{\pi C^{11}}\{C\cosh(C)[C(C^8 + 990C^6 + 135135C^4 + 4729725C^2 + 34459425)\omega - (46C^8 + 16830C^6 + 1621620C^4 + 49324275C^2 + 344594250)\sigma] + \sinh(C)[(C^{10} + 1080C^8 + 190575C^6 + 10405395C^4 + 164189025C^2 + 344594250)\sigma - 45C(C^8 + 308C^6 + 21021C^4 + 360360C^2 + 765765)\omega]\}, \tag{A21}$$

$$\Sigma_0^{10} = \frac{2}{\pi C^{12}}\{\sinh(C)[C(C^{10} + 1485C^8 + 315315C^6 + 18918900C^4 + 310134825C^2 + 654729075)\omega - (56C^{10} + 30195C^8 + 4414410C^6 + 224324100C^4 + 3445942500C^2 + 7202019825)\sigma] + C\cosh(C)[(C^{10} + 1595C^8 + 418275C^6 + 35945910C^4 + 1045269225C^2 + 7202019825)\sigma - 55C(C^8 + 468C^6 + 51597C^4 + 1670760C^2 + 11904165)\omega]\}, \tag{A22}$$

$$\Xi_0^0 = 0, \tag{A23}$$

$$\Xi_0^1 = 2\Upsilon_0^1, \tag{A24}$$

$$\Xi_0^2 = 6\Upsilon_0^2, \tag{A25}$$

$$\Xi_0^3 = 12\Upsilon_0^3, \tag{A26}$$

$$\Xi_0^4 = 20\Upsilon_0^4, \tag{A27}$$

$$\Xi_0^5 = 30\Upsilon_0^5. \tag{A28}$$

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