Deformed Explicitly Correlated Gaussians

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Deformed correlated Gaussian basis functions are introduced and their matrix elements are calculated. These basis functions can be used to solve problems with nonspherical potentials. One example of such potential is the dipole self-interaction term in the Pauli-Fierz Hamiltonian. Examples are presented showing the accuracy and necessity of deformed Gaussian basis functions to accurately solve light-matter coupled systems in cavity QED.

I. INTRODUCTION

Few-body approaches have reached very high accuracy in atomic and molecular systems1–19 and these calculations proved to be indispensable explaining properties such as the electron correlations20, relativistic effects21,22, molecular bonds22–24, and quantum dynamics of nuclei25–28. As an example, the accuracy of theoretical prediction29 and experimental measurements30 has reached the level of 1 MHz for the dissociation energy of the H2 molecule. The accuracy allows benchmarking the theory against measurement to answer fundamental questions (e.g. about the nature of the physical constants) and the development of accurate approximations for efficient computational approaches.

Not all few-body approaches are created equal. There are approaches with distinct advantages for certain systems and well-known limitations for others. Hylleraas-type wave functions work extremely well in two- and three-electron atomic systems31–34 but the extension of the Hylleraas basis approach beyond three electrons is very tedious because the analytical calculation of the matrix elements35 is difficult. Hyperspherical approaches36–42 have also been successfully used but have similar limitations although there are new approaches to circumvent the size restrictions43–45.

The matrix elements of Explicitly Correlated Gaussian (ECG) can be calculated for any number of particles. Because of this, ECGs became very popular tools in high accuracy calculations.10,15–17,19,55–90. The practice of using ECGs as basis functions has been around since 1960.12. The quadratic form involving inter-particle distances in ECGs permits the reduction of the Hamiltonian matrix elements to very simple analytic expressions and the algebraic complexity of the matrix elements does not change with the number of particles. Further, the matrix elements can be generalized for an arbitrary angular momentum59,68,82,90,97,98. These matrix elements depend on the Gaussian parameters of the ECGs which should be carefully optimized59,78,85,97,100 to get highly accurate variational upper bounds. The Gaussian parameters are most often chosen to be real, but the extension to complex parameters has also been tested.48,93,106 Systems with periodic boundary conditions have also been investigated.197

The wide range of applications of ECGs has been demonstrated in several recent reviews.17,58,62. Currently, high accuracy ECG calculations are actively pursued for relatively large systems, e.g. five-body calculations of the energy of the H5+ or the Beryllium atom with finite nuclei mass57, or a six-particle calculation of the Boron atom156 and the singly charged Carbon ion155. These calculations reached high accuracy, and using relativistic corrections are comparable to the experimental data. To reach this accuracy for large systems one needs a large basis dimension. For example, in Ref.57, 16000 basis functions were used. Additionally, ECGs have been applied to the nuclei in multi-cluster approximations.108,109,113. While these cases do not reach the same level of accuracy as the atomic and molecular cases, ECGs offer the unique advantage of treating the nuclear dynamics in an efficient way.

The ECGs are not restricted to bound state problems. More recently scattering of composite particles have also been studied using ECG’s combined with the confined variational method.114–122.

There are many works that have evaluated the matrix elements of ECG’s for spherical (L = 0) cases.96,100,105,122,126. Spherical ECGs have been used in a variety of applications, such as the study of Efimov physics58, hyperfine splitting127, quantum electrodynamic corrections68, Fermi gases of cold atoms128, and potential energy curves61.

There are many systems where nonspherical (L > 0) ECGs are necessary (e.g. polyatomic molecules or excited states of atoms), but the calculation of the matrix elements of these functions is more complicated. There are two different ways that have been proposed. In the first one the Gaussian centers are shifted, which introduces nonspherical components into the basis functions.59,78,85,86,100,128. The advantage of this approach is that the calculation of the matrix elements remain simple, and the disadvantage is that the desired angular momentum has to be built-in59,77,129 or has to be projected out.78,85.

The second possibility is to multiply the ECGs with polynomials of the interparticle coordinates. Different approaches have been developed to calculate the matrix elements in this case. For example, one can restrict the calculation for a special L value, and explicitly work out the formalism for that case. For example, Refs.20,194,195,197 calculated the energy and energy
gradient matrix elements for $L = 1$, while Ref.\textsuperscript{130} tackled D states. Alternatively, representations using “global vectors” have been put forward\textsuperscript{69,75,108} and this approach has been developed further.\textsuperscript{69,75,108} In the global vector representation, a vector $\mathbf{v}$, formed as a linear combination of all particle coordinates, is used as an argument of spherical harmonics to define the orbital momentum. The coefficients in the linear combination are treated as real-valued variational parameters. The advantage of this approach is that the calculation of the matrix elements remains relatively simple. The disadvantage of this approach is that the calculation of the overlap matrix, dipole self-interaction removal, electron-photon coupling in addition to the kinetic and potential energy operators. Numerical examples are given in Sect. \textsuperscript{III} To make the paper more easily readable, useful but not essential equations are collected in the Appendices. Atomic units are used in the paper.

II. FORMALISM

We consider a system of $N$ particles with positions $\mathbf{r}_1, ..., \mathbf{r}_N$, where $\mathbf{r}_i = (x_i, y_i, z_i)$, and charges $q_1, ..., q_N$. We define

$$
\mathbf{x} = \begin{pmatrix}
x_1 \\
x_2 \\
\vdots \\
x_N
\end{pmatrix}
$$

and $\mathbf{y}$ and $\mathbf{z}$ similarly. We also define

$$
\mathbf{r} = \begin{pmatrix}
x \\
y \\
z
\end{pmatrix}
= \begin{pmatrix}
x_1 \\
x_2 \\
\vdots \\
x_N
\end{pmatrix}
= \begin{pmatrix}
r_1 \\
r_2 \\
\vdots \\
r_N
\end{pmatrix}
$$

So in the following $\hat{a}$ will be used for 3-dimensional vectors, and $\mathbf{a}$ will be used for a set of single-particle coordinates in a given direction as defined by Eq. (1), and $\mathbf{r}$ is a three dimensional vector formed by a set of single-particle coordinates.

A simple form of DECG functions are defined as

$$
\exp \left\{ -\frac{1}{2} \hat{x} A_{xz} x - \frac{1}{2} \hat{y} A_{yz} y - \frac{1}{2} \hat{z} A_{zz} z \right\}
\times \exp \left\{ -\hat{x} A_{xy} y - \hat{y} A_{yz} z - \hat{z} A_{zz} z \right\},
$$

where $x, y, z$ are single-particle coordinates.
where \(A_{\alpha \beta}\) are \(N \times N\) symmetric matrices. The scalar (inner) product \((\hat{a} \cdot \hat{b})\) for \(N\)-dimensional vectors \(\hat{a} = (a_1, a_2, ..., a_N)\) and \(\hat{b} = (b_1, b_2, ..., b_N)\) is to be understood as \((\hat{a} \cdot \hat{b}) = \sum_{m=1}^{N} a_m b_m\). Assuming \(A_{xx} = A_{yy} = A_{zz} = \lambda\) and \(A_{xy} = A_{zx} = A_{yz} = 0\), one gets back the original definition of ECGs.

Now we can define the block matrix \(A\) as

\[
A = \begin{pmatrix}
A_{xx} & A_{xy} & A_{xz} \\
A_{xy} & A_{yy} & A_{yz} \\
A_{xz} & A_{yz} & A_{zz}
\end{pmatrix},
\]

and the DECG function can be written as

\[
\exp \left\{ -\frac{1}{2} \tilde{r} A^k \tilde{r} \right\},
\]

where the tilde is dropped for simplicity. The superscript \(k\) stands for the \(k\)-th basis function and

\[
\tilde{r} A^k \tilde{r} = \sum_{i,j=1}^{3N} r_i A_{ij}^k r_j.
\]

We multiply the simple DECG by

\[
\exp \{ \tilde{r} \hat{s} \} = \exp \left\{ \sum_{i=1}^{3N} s_i \tilde{r}_i \right\},
\]

to form a basis that can describe nonzero angular momentum states and systems of multiple centers (molecules):

\[
\Psi_k = \exp \left\{-\frac{1}{2} \tilde{r} A^k \tilde{r} + \tilde{r} \hat{s}^k \right\}.
\]

As an example, assume that we write the trial function in the following form

\[
\exp \left\{ -\frac{1}{2} \sum_{i<j}^N \alpha_{ij}^x (x_i - x_j)^2 - \frac{1}{2} \sum_{i<j}^N \alpha_{ij}^{yy} (y_i - y_j)^2 - \frac{1}{2} \sum_{i<j}^N \alpha_{ij}^{zz} (z_i - z_j)^2 \right\}
\]

\[
\times \exp \left\{ -\frac{1}{2} \sum_{i,j=1}^{3N} \alpha_{ij}^x (x_i - x_j)^2 - \frac{1}{2} \sum_{i,j=1}^{3N} \alpha_{ij}^{xy} (x_i - x_j)(y_i - y_j) - \frac{1}{2} \sum_{i,j=1}^{3N} \alpha_{ij}^{yz} (y_i - y_j)(z_i - z_j) - \frac{1}{2} \sum_{i=1}^{3N} \beta_i (\tilde{r}_i - \tilde{c}_i)^2 \right\}.
\]

In this case, we have a correlation between the particle coordinates and a single particle function centered at \(\tilde{c}_i\). The relation between the coefficients in Eq. (4) and Eq. (9) is shown in Appendix A.

### A. Hamiltonian

The Hamiltonian of the system is

\[
H = H_e + H_{ph} = H_e + H_p + H_{ep} + H_d.
\]

\(H_e\) is the electronic Hamiltonian, and \(H_p\) is the photon Hamiltonian. The electron-photon coupling is denoted as \(H_{ep}\), and the dipole self-interaction is \(H_d\). In this case the electron-photon interaction is described by using the PF nonrelativistic QED Hamiltonian. The PF Hamiltonian can be derived by applying the Power-Zienau-Woolley gauge transformation, with a unitary phase transformation on the minimal coupling \((p \cdot A)\) Hamiltonian in the Coulomb gauge,

\[
H_{ph} = \frac{1}{2} \sum_{\alpha=1}^{N_q} \left( p_{\alpha}^2 + \omega_{\alpha}^2 \left( q_{\alpha} - \frac{\tilde{r}}{\omega_{\alpha}} \cdot \vec{D} \right) \right)^2,
\]

where \(\vec{D}\) is the dipole operator. The photon fields are described by quantized oscillators. \(q_{\alpha} = \frac{1}{\sqrt{2 \omega_{\alpha}}} (a_{\alpha}^\dagger + a_{\alpha})\) is the displacement field and \(p_{\alpha}\) is the conjugate momentum. This Hamiltonian describes \(N_p\) photon modes with frequency \(\omega_{\alpha}\) and coupling \(\lambda_{\alpha}\). The coupling term is usually written as

\[
\lambda_{\alpha} = \sqrt{4 \pi S_{\alpha}(\tilde{r}) c_{\alpha}},
\]

where \(S_{\alpha}(\tilde{r})\) is the mode function at position \(\tilde{r}\) and \(c_{\alpha}\) is the transversal polarization vector of the photon modes.

The electronic Hamiltonian is the usual Coulomb Hamiltonian and the three components of the electron-photon interaction are as follows: The photonic part is

\[
H_p = \sum_{\alpha=1}^{N_p} \left( \frac{1}{2} p_{\alpha}^2 + \omega_{\alpha}^2 a_{\alpha} a_{\alpha}^\dagger \right) = \sum_{\alpha=1}^{N_p} \omega_{\alpha} \left( a_{\alpha}^\dagger a_{\alpha} + \frac{1}{2} \right),
\]

and the interaction term is

\[
H_{ep} = - \sum_{\alpha=1}^{N_p} \omega_{\alpha} q_{\alpha} \lambda_{\alpha} \cdot \vec{D} = - \sum_{\alpha=1}^{N_p} \sqrt{\frac{\omega_{\alpha}}{2} (a_{\alpha} a_{\alpha}^\dagger + a_{\alpha}^\dagger a_{\alpha})} \lambda_{\alpha} \cdot \vec{D}.
\]
Only photon states $|n_\alpha\rangle$, $|n_\alpha \pm 1\rangle$ are connected by $\hat{a}_\alpha$ and $\hat{a}_\alpha^\dagger$. The matrix elements of the dipole operator $\hat{D}$ are only nonzero between spatial basis functions with angular momentum $l$ and $l \pm 1$ in 3D or $m$ and $m \pm 1$ in 2D.

The dipole self-interaction is defined as

$$H_d = \frac{1}{2} \sum_{\alpha=1}^{N_c} \left( \hat{a}_\alpha^\dagger \cdot \vec{D} \right)^2,$$  \hspace{1cm} (15)

and the importance of this term for the existence of a ground state is discussed in Ref. \textsuperscript{154}.

In the following, we will assume that there is only one important photon mode with frequency $\omega$ and coupling $\lambda$. Thus the suffix $\alpha$ is omitted in what follows. The formalism can be easily extended for many photon modes but here we concentrate on calculating the matrix elements and it is sufficient to use a single-mode.

For one photon mode Eqs. \textsuperscript{13} \textsuperscript{14} and \textsuperscript{15} can be simplified and the Hamiltonian becomes

$$H = T + V + U + \omega \left( \hat{a}^\dagger \hat{a} + \frac{1}{2} \right) + \omega \vec{X} \cdot \vec{D} q + \frac{1}{2} (\vec{X} \cdot \vec{D})^2,$$  \hspace{1cm} (16)

where $T$ is the kinetic operator

$$T = -\frac{1}{2} \sum_{i=1}^{N} \left( \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right).$$  \hspace{1cm} (17)

$V$ is the Coulomb interaction

$$V = \sum_{i<j} V_c(\vec{r}_i - \vec{r}_j), \hspace{1cm} V_c(\vec{r}_i - \vec{r}_j) = \frac{q_i q_j}{|\vec{r}_i - \vec{r}_j|},$$  \hspace{1cm} (18)

$U$ is an external potential

$$U = \sum_{i=1}^{N} U(\vec{r}_i),$$  \hspace{1cm} (19)

and the dipole moment $\vec{D}$ of the system is defined as

$$\vec{D} = \sum_{i=1}^{N} q_i \vec{r}_i.$$  \hspace{1cm} (20)

The operators act in real space, except $q$ which acts on the photon space

$$q | n \rangle = \frac{1}{\sqrt{2\omega}} (a + a^\dagger) | n \rangle = \frac{1}{\sqrt{2\omega}} \left( \sqrt{n} | n - 1 \rangle + \sqrt{n+1} | n + 1 \rangle \right).$$  \hspace{1cm} (21)

In the following, we calculate the matrix elements of DECGs. Most of the matrix elements calculated previously for ECGs remain the same except the one that uses the DECG block matrix.

**B. Overlap matrix**

The overlap matrix is given by

$$\langle \Psi_i | \Psi_j \rangle = \int \exp \left\{ -\frac{1}{2} \vec{A} \vec{r} + \vec{r} \vec{s} \right\} d\vec{r},$$  \hspace{1cm} (22)

where $A$ and $\vec{s}$ are defined as

$$A = A^i + A^j, \hspace{1cm} \vec{s} = \vec{s}^i + \vec{s}^j,$$  \hspace{1cm} (23)

and can be calculated using Eq. \textsuperscript{112} in Appendix \textsuperscript{13}

$$\langle \Psi_i | \Psi_j \rangle = \frac{(2\pi)^{3N/2}}{(\det A)^{1/2}} \exp \left\{ -\frac{1}{2} \vec{s} A^{-1} \vec{s} \right\}.$$  \hspace{1cm} (24)

**C. Kinetic energy**

We will write the kinetic energy operator in the following form

$$T = \vec{p} \Lambda \vec{p},$$  \hspace{1cm} (25)

where the momentum operator is given by

$$p_i = -i \hbar \frac{\partial}{\partial r_i} \hspace{1cm} (i = 1, \ldots, 3N).$$  \hspace{1cm} (26)

For a system of particles with masses $m_1, \ldots, m_N$, $\Lambda$ is a block diagonal matrix

$$\Lambda = \begin{pmatrix} \Lambda^x & 0 & 0 \\ 0 & \Lambda^y & 0 \\ 0 & 0 & \Lambda^z \end{pmatrix},$$  \hspace{1cm} (27)

where the matrix elements of the block diagonal matrix are given by

$$\Lambda^\alpha_{ij} = \frac{1}{2m_i} \delta_{ij},$$  \hspace{1cm} (28)

for systems where the external potential fixes the center of the system (e.g. electrons in a harmonic oscillator potential, or electrons in an atom where the mass of the nucleus is taken to be infinity). Otherwise, we have to remove the center of mass motion of the system using

$$\Lambda^\alpha_{ij} = \frac{1}{2m_i} \delta_{ij} - \frac{1}{2M},$$  \hspace{1cm} (29)

where $M = m_1 + m_2 + \ldots m_N$. In principle $\Lambda^x$, $\Lambda^y$ and $\Lambda^z$ can be different if the masses of particles depend on the directions.

Taking the derivative on the right-hand side
\[ \frac{\partial}{\partial r_i} \exp \left\{ -\frac{1}{2} \bar{r} A^i \bar{r} + \bar{r} \tilde{s} \right\} = \left( -\left( A^i \bar{r} \right)_i + s_i \right) \exp \left\{ -\frac{1}{2} \bar{r} A^i \bar{r} + \bar{r} \tilde{s} \right\}. \]  

(30)

Using analogous results on the left side, the overlap with the kinetic energy operator can be given by

\[ \langle \Psi_i | T | \Psi_j \rangle = \int \left( \bar{r} \left( A^i \Lambda A^j \right) \bar{r} + \tilde{s}^i \Lambda \tilde{s}^j - \tilde{s}^i \Lambda A^j \bar{r} - A^i \bar{r} \Lambda \tilde{s}^j \right) \exp \left\{ -\frac{1}{2} \bar{r} A^i \bar{r} + \bar{r} \tilde{s} \right\} d\bar{r} 
= \left( \text{Tr}(A^i \Lambda A^j A^{-1}) - \tilde{y} A \tilde{y} \right) \langle \Psi_i | \Psi_j \rangle, \]  

(31)

where we used Eqs. (33) and (34) and define \( \tilde{y} \) as

\[ \tilde{y} = A^i A^{-1} \tilde{s}^i - A^i A^{-1} \tilde{s}^j. \]  

(32)

### D. Potential energy

Both \( V_c \) and \( U \) can be rewritten using a \( \delta \) function,

\[ V_c(\bar{r}^i - \bar{r}^j) = \int \delta(\bar{w}^{ij} \bar{r} - \bar{r}) V_c(\bar{r}) d\bar{r}, \]  

(33)

where \( \bar{w}^{ij} \bar{r} \) is a short-hand notation for \( \sum_{k=1}^{N} w_k^{ij} r_k \) and in this case \( w_k^{ij} = \delta_{ik} - \delta_{jk} \). The corresponding formula for \( U \) is

\[ U(\bar{r}^i) = \int \delta(\bar{w}^{ij} \bar{r} - \bar{r}) U(\bar{r}) d\bar{r}, \]  

(34)

We want to calculate the matrix elements

\[ \langle \Psi_i | \delta(\bar{w} \bar{r} - \bar{r}) | \Psi_j \rangle = \frac{1}{(2\pi)^3} \int \int e^{i\bar{k}(\bar{w} \bar{r} - \bar{r})} \exp \left\{ -\frac{1}{2} \bar{r} A^i \bar{r} + \bar{r} \tilde{s} \right\} d\bar{r} d\bar{k}. \]  

(36)

Using Eq. (32), we can express the matrix element as

\[ \langle \Psi_i | \delta(\bar{w} \bar{r} - \bar{r}) | \Psi_j \rangle = \frac{1}{(2\pi)^3} \left( \frac{(2\pi)^{3N}}{\det A} \right)^{\frac{1}{2}} \int e^{-i\bar{k} \bar{r}} \exp \left( \frac{1}{2} \bar{t} A^{-1} \bar{t} \right) d\bar{k} \]  

\[ = \frac{1}{(2\pi)^3} \left( \frac{(2\pi)^{3N}}{\det A} \right)^{\frac{1}{2}} \int e^{-i\bar{k} \bar{r}} \exp \left( -\frac{1}{2} \bar{k} B \bar{k} + \frac{1}{2} \tilde{s} A^{-1} \tilde{s} + i\bar{k} \tilde{s} \right) d\bar{k}, \]  

(38)

where \( B \) is a \( 3 \times 3 \) matrix given by

\[ B = \begin{pmatrix} B_{11} & B_{12} & B_{13} \\ B_{12} & B_{22} & B_{23} \\ B_{13} & B_{23} & B_{33} \end{pmatrix}, \]  

(39)

with the matrix elements of \( B \) defined as

\[ B_{ij} = \sum_{k=(i-1)N+1}^{iN} \sum_{l=(j-1)N+1}^{jN} w_k A^{-1}_{kl} w_l, \]  

(40)
where \( k' = k - (i - 1) \cdot N \) and \( l' = l - (j - 1) \cdot N \). We have also defined a three dimensional vector \( \vec{b} \):

\[
b_i = \sum_{k=(i-1) \cdot N+1}^{i \cdot N} w_{k'} \left( A^{-1} \vec{s} \right)_k.
\]

Integrating over \( \vec{r} \) should give back the overlap, and using Eq. (42) one immediately gets these results. Note that Eq. (42) can also be used to calculate the single particle density. This formula is generalized for two particle density in Appendix B.

E. Electron-photon coupling

By introducing \( \vec{q} \) as

\[
\vec{q} = \begin{pmatrix}
\lambda_1 q_1 \\
\lambda_1 q_2 \\
\vdots \\
\lambda_2 q_N \\
\lambda_3 q_1 \\
\vdots \\
\lambda_3 q_N
\end{pmatrix},
\]

the relevant part of the coupling term can be written as

\[
\vec{\lambda} \cdot \vec{D} = \vec{q} \vec{r},
\]

and the matrix elements of this term can be easily calculated using Eq. (B3):

\[
\langle \Psi_i | \vec{\lambda} \cdot \vec{D} | \Psi_j \rangle = \int \vec{\lambda} \cdot \vec{D} \exp \left\{ -\frac{1}{2} \vec{r}^\dagger A \vec{r} + \vec{r} \vec{s} \right\} d\vec{r} = \vec{q} A^{-1} \vec{s} \langle \Psi_i | \Psi_j \rangle.
\]

F. Dipole self-interaction

The dipole self-interaction term is a special quadratic form and this quadratic form can be represented with DECG exponent. One can try to find a suitable DECG exponent. One can try to find a suitable DECG exponent. One can try to find a suitable DECG exponent. One can try to find a suitable DECG exponent.

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G. Eliminating the dipole self-interaction

One motivation of DECG is that the dipole self-interaction term of the Hamiltonian can be eliminated using a special choice of DECG exponentials producing a much simpler Hamiltonian.

The dipole self-interaction term is a special quadratic form and this quadratic form can be represented with DECG exponent. One can try to find a suitable DECG exponent. One can try to find a suitable DECG exponent. One can try to find a suitable DECG exponent.

To solve this we need to evaluate the second derivative of the exponential with respect to \( \vec{r}_i \). The first derivative with respect to \( x_i \) is given by

\[
\frac{\partial}{\partial x_i} \exp \left( \alpha (\vec{\lambda} \cdot \vec{D})^2 \right) = 2 \alpha \lambda_i q_i (\vec{\lambda} \cdot \vec{D}) \exp \left( \alpha (\vec{\lambda} \cdot \vec{D})^2 \right),
\]

and the second derivative

\[
\frac{\partial^2}{\partial x_i^2} \exp \left( \alpha (\vec{\lambda} \cdot \vec{D})^2 \right) = 2 \alpha \lambda_i^2 q_i^2 \exp \left( \alpha (\vec{\lambda} \cdot \vec{D})^2 \right) + 4 \alpha^2 \lambda_i^3 q_i (\vec{\lambda} \cdot \vec{D}) \exp \left( \alpha (\vec{\lambda} \cdot \vec{D})^2 \right),
\]

with similar expressions for \( y_i \) and \( z_i \). By choosing \( \alpha \) as

\[
\alpha = \frac{1}{2 \sqrt{\sum_{i=1}^N \lambda_i q_i^2}},
\]

where \( \lambda \) is the magnitude of \( \vec{\lambda} \), we can express the kinetic energy operator acting on the exponential as

\[
\langle \Psi_i | \frac{1}{2} (\vec{\lambda} \cdot \vec{D})^2 | \Psi_j \rangle = \frac{1}{2} \left( \vec{q} A^{-1} \vec{q} + (\vec{q} A^{-1} \vec{s})^2 \right) \langle \Psi_i | \Psi_j \rangle.
\]
This means that by multiplying the basis with the factor
\[ \exp\left(\alpha (\vec{\lambda} \cdot \vec{D})^2\right), \tag{52} \]
the dipole self-interaction can be removed and the numerical solution is much simpler. In this way, the nonspherical dipole self-interaction is eliminated. In other words, it is built in the basis functions. Note that the above exponential form can be recast into a DECG, but not into an ECG. The generalization of Eq. \texttt{(51)} to multiphoton mode can be found in Appendix \texttt{E}.

### III. NUMERICAL EXAMPLES

In this section, we present a few numerical examples to show that the matrix elements evaluated in this paper can be used in practical calculations. We will not fully explore the efficiency of the DECG basis, and we restrict our approach to an \( A \) matrix of the form
\[ A = \begin{pmatrix} A_{xx} & 0 & 0 \\ 0 & A_{xx} & 0 \\ 0 & 0 & A_{xx} \end{pmatrix}, \tag{53} \]
and the trial function is
\[ \Psi_k = \exp\left\{-\frac{1}{2} \vec{r}^2 (A^k + 2\alpha (\vec{\lambda} \cdot \vec{D})) + \vec{r}^2 \right\}, \tag{54} \]
where \( \alpha \) is defined in Eq. \texttt{(50)}. If \( \alpha = 0 \) then this function is the conventional ECG basis function. Nonzero \( \alpha \) leads to nonzero off diagonal block matrices and the basis becomes DECG.

In these calculations, we have used the separable approximation of \( 1/r \) in terms of Gaussians\textsuperscript{152}.
\[ \frac{1}{r} = \sum_k w_k e^{-p_k r^2}. \tag{55} \]
In this way, the integral in Eq. \texttt{(42)} can be analytically evaluated (a numerical approach is presented in Appendix \texttt{C}). 89 Gaussian functions with the coefficients \( w_k \) and \( p_k \) (taken from Ref.\textsuperscript{153}) can approximate \( 1/r \) with an error less than \( 10^{-9} \) in the interval [10\textsuperscript{-9}, 1]a.u. For larger intervals, one can easily scale to coefficients. Note that this expansion uses significantly fewer terms than a Gaussian quadrature for the same accuracy\textsuperscript{154}.

As a first example, we consider a 2D system of 2 electrons in a harmonic oscillator confinement potential,
\[ \frac{1}{2} \sum_{i=1}^{2N} \frac{\partial^2}{\partial x_i^2} + \frac{2}{r_i^2}, \tag{56} \]
interacting via a Coulomb potential. This problem is analytically solvable\textsuperscript{155} and we will compare the ECG (\( \alpha = 0 \)) and DECG solutions. We take \( \omega = 0 \) in Eq. \texttt{(19)}, so there is no coupling to photons but the potential is nonspherical because \( \lambda \neq 0 \). We test two \( \lambda \) values: \( \lambda = 1 \) a.u. (the energy is \( E = 2.7807764 \) a.u.) and \( \lambda = 2.5 \) (\( E = 4.2624689 \)). Fig. \texttt{1} shows the convergence of energy as a function of the number of basis states. Each basis state is selected by comparing 250 random parameter sets and choosing the one that minimizes the energy. The DECG converges up to 3-4 digits on a basis of 100 states. The ECG converges much slower, and for the stronger coupling (\( \lambda = 2.5 \)) the energy is 0.9 a.u. above the exact value. A larger basis dimension and more parameter optimizations would improve the results, but this already shows the general tendency and the superiority of the DECG basis. Note, that the ECG would also converge to the exact result after more optimization and much larger basis size.

The next example is a 2D \( H_2 \) molecule with nuclei fixed at distance \( r \). In this case, we assume that there is only one relevant photon mode with frequency \( \omega = 1.5 \) a.u. There are infinitely many photons with energy \( n\hbar \omega \) \((n = 0, 1, 2, \ldots)\), but only the lowest photon states are coupled to the electronic part. We solve Eq. \texttt{(19)} using the lowest \( n = 0, \ldots, 5 \) photon spaces. The energy of a 2D \( H \) atom is \( E = -2 \) a.u. without coupling the photons. The energy of the atom coupled to photons with \( \lambda = 1 \) a.u. increases to \( E = -1.71 \) a.u. The increase is largely due to the dipole self energy part in Eq. \texttt{(19)}. The probability amplitudes of the spatial wave function in photon spaces are 0.988 (\( n = 0 \)), 0.01 (\( n = 1 \)) and 0.001 \( n = 2 \). These are small probabilities but there is a relatively strong coupling between the electrons and light. This is shown by the fact that the energy without coupling (solely due to the dipole self-interaction and the Coulomb) is -1.67 a.u. By increasing the coupling further the energy of the \( H_2 \) increases (e.g. for \( \lambda = 3 \), \( E=-1.15 \) a.u.).

Fig. \texttt{2} shows the energy of the \( H_2 \) molecule with and without coupling to light. Without coupling to light, the 2D \( H_2 \) molecule has a lowest energy at around \( r = 0.35 \) a.u. The the \( H_2 \) molecule to light the energy minimum slightly shifts toward shorter distances. Overall the three curves are very similar except that the dipole self-interaction term pushes them higher with increasing \( \lambda \). The binding energies at the minimum energy point increase with \( \lambda \): \( E_0 = 1.34 \) a.u. (\( \lambda = 0 \)), \( E_0 = 1.47 \) (\( \lambda = 1 \) a.u.), and \( E_0 = 1.68 \) a.u. (\( \lambda = 3 \) a.u.), where \( E_0 \) is the difference of the energy of the molecule and two times the energy of the H atom.

The final example is the \( H^- \) ion with finite (\( m_H = \)}
1836.1515 a.u.) and infinite nuclear mass in 3D. Fig. 3 shows the energy of the H atom and H− ion as a function of λ. As the figure shows, the H− dissociates for strong λ in the finite mass case but remains stable in the infinite mass case. In the finite mass case, the dissociation happens around λ = 0.08 a.u., at that point, the energy of the H plus an electron system becomes lower than that on H− (the energy of the electron coupled to light is calculated by solving Eq. (16) for the electron). This example shows the importance of explicit treatment of the system as a three-body system because the light strongly couples to the proton as well.

IV. SUMMARY

We have introduced a new variant of ECG basis functions that are suitable for problems with nonspherical potentials. All necessary matrix elements are calculated and numerically tested. The treatment of the Coulomb interaction is more complicated than in the conventional ECG case due to the nonspherical integrals that appear in the interaction part. Two ways are proposed to solve this problem. One can either expand the Coulomb potential in Gaussians and the integration becomes analytical, or use numerical integration.

We have shown that using the DECG basis the coupled light-matter equations can be efficiently solved even when the coupling and thus the dipole self-interaction term is large. This opens up the way to calculate light-matter coupled few-body systems with high accuracy in cavity QED systems.

Appendix A: Relating different forms of basis functions

In this appendix we show how Eq. (8) and Eq. (9) can be related and how the matrix elements of the trial function can be determined.
\[
\Psi = \exp \left\{ -\frac{1}{2} \sum_{i<j}^N \alpha_{ij}^x (x_i - x_j)^2 - \frac{1}{2} \sum_{i<j}^N \alpha_{ij}^y (y_i - y_j)^2 - \frac{1}{2} \sum_{i<j}^N \alpha_{ij}^z (z_i - z_j)^2 \right\} \\
\times \exp \left\{ -\frac{1}{2} \sum_{i,j=1}^N \alpha_{ij}^{xy} (x_i - y_j)^2 - \frac{1}{2} \sum_{i,j=1}^N \alpha_{ij}^{xz} (x_i - z_j)^2 - \frac{1}{2} \sum_{i,j=1}^N \alpha_{ij}^{yz} (y_i - z_j)^2 - \frac{1}{2} \sum_{i=1}^N \beta_i (\vec{r}_i - \vec{c}_i)^2 \right\}.
\]

(A1)

The diagonal blocks of the trial function evaluate to

\[
\sum_{i<j}^N \alpha_{ij}^x (x_i - x_j)^2 = x M_{xx} x,
\]

(A2)

where \( M_{xx} \) is an \( N \times N \) symmetric matrix:

\[
(M_{xx})_{ij} = \begin{cases} \sum_{k=1}^N \alpha_{ik}^x, & (M_{xx})_{ij} = -\alpha_{ij}^x \text{ for } i \neq j. 
\end{cases}
\]

(A3)

Here, \( \alpha_{ij}^x \) for \( j > i \) is set equal to \( \alpha_{ij}^x \). The off-diagonal blocks of the trial function evaluate to

\[
\sum_{i,j=1}^N \alpha_{ij}^{xy} (x_i - y_j)^2 = x G_{xx}^{xy} x + y G_{yy}^{xy} y + x G_{xy}^{xy} y + y G_{yy}^{xy} x,
\]

(A4)

where \( G_{xx}^{xy} \) and \( G_{yy}^{xy} \) are both diagonal,

\[
(G_{xx}^{xy})_{ii} = \sum_{j=1}^N \alpha_{ij}^{xy},
\]

\[
(G_{yy}^{xy})_{ij} = \sum_{j=1}^N \alpha_{ij}^{xy}.
\]

(A5)

Here, \( \vec{s} = (\beta_1 c_1, \beta_2 c_2, \ldots, \beta_{NcN_x}, \beta_1 c_1, \beta_2 c_2, \ldots, \beta_{NcN_x}, \beta_1 c_1, \beta_2 c_2, \ldots, \beta_{NcN_x}) \). Combining the above results leads to

\[
\Psi = \exp \left\{ -\frac{1}{2} \vec{r}^T A \vec{r} + \vec{s} \cdot \vec{r} - \frac{1}{2} \sum_{i=1}^N \beta_i \vec{c}_i \cdot \vec{c}_i \right\},
\]

(A9)

with the matrix \( A \) given by

\[
A = \begin{pmatrix}
M_{xx} + G_{xx}^{xy} + G_{xx}^{xz} + B & G_{yy}^{xy} & G_{yz}^{xy} \\
G_{xy}^{xy} & M_{yy} + G_{yy}^{xy} + G_{yy}^{yz} + B & G_{yz}^{yy} \\
G_{xz}^{xy} & G_{yz}^{yx} & M_{zz} + G_{zz}^{xz} + G_{zz}^{yz} + B
\end{pmatrix}.
\]

(A10)

Comparing \( A \) with Eq. (B4), one obtains \( A_{\alpha\beta} \). For example,

\[
A_{xx} = M_{xx} + G_{xx}^{xy} + G_{xx}^{xz} + B, \quad A_{xy} = G_{xy}^{xy}.
\]

(A11)

and their matrix elements are easily obtained from the above defining equations.

Appendix B: Generalized Gaussian integrals

In this appendix, we list the most important formulas for Gaussian integrals. These results are valid in \( n = d \times N \) dimension, where \( d \) is the space dimension. Define the generating function
TABLE I: Matrix elements, $M = \langle g(\vec{s}; A', \vec{r}) | O | g(\vec{s}; A, \vec{r}) \rangle$, of operators $O$ between generating functions $g$ of Eq. (B1). Here we take all vectors $d$-dimensional. $\hat{\vec{w}}\vec{r}$ is a short-hand notation for $\sum_{i=1}^{N} w_i \vec{r}_i$. $B = A + A'$, $\vec{v} = \vec{s} + \vec{s}'$, $\vec{y} = A'B^{-1} \vec{s} - AB^{-1} \vec{s}'$ where the elements of $w_i$ from 1 to $N$ are repeated for $N + 1$ to $2N$ and $2N + 1$ to $3N$. $P$ is a permutation operator and the matrix $T_P$ is defined by $P\vec{r} = T_P\vec{r}$. Additionally, we define both $Q$ and $\Lambda$ as symmetric matrices.

| $O$ | $M$ |
|---|---|
| $1$ | $M_0 \equiv \left( \frac{2\pi)^n}{\det A} \right)^{\frac{1}{2}} \exp\left( \frac{1}{2} \hat{\vec{v}} B^{-1} \hat{\vec{v}} \right)$ |
| $\hat{\vec{w}}\vec{r}$ | $\hat{\vec{w}} B^{-1} \hat{\vec{v}} M_0$ |
| $\hat{\vec{r}} Q \vec{r}$ | $\left\{ \text{Tr}(B^{-1} Q) + \hat{\vec{v}} B^{-1} Q B^{-1} \hat{\vec{v}} \right\} M_0$ |
| $\hat{\vec{r}} \vec{\zeta} \vec{r}$ | $-i\hbar \hat{\vec{y}} M_0$ |
| $(\pi_j = \frac{-i\hbar}{\vec{r}_j})$ | $\hat{\vec{y}} \vec{\Lambda} \hat{\vec{y}}$ |
| $\delta(\hat{\vec{w}}\vec{r} - \vec{r})$ | $M_1 \equiv \left( \frac{2\pi)^n}{\det A} \right)^{\frac{1}{2}} \times \exp\left( \frac{-1}{2} \hat{\vec{w}} B^{-1} \hat{\vec{w}} \right) M_0$ |
| $P$ | $\langle g(\vec{s}; A', \vec{r}) | g(T_P \vec{s}; T_P A T_P, \vec{r}) \rangle$ |

Further differentiation with respect to $\vec{s}_j$ leads us to

$$g(\vec{s}, A, \vec{r}) = \exp\left( -\frac{1}{2} \vec{r} A \vec{r} + \vec{s} \vec{r} \right). \quad (B1)$$

The evaluation of a Gaussian integral of this form is given by

$$\int \exp\left( -\frac{1}{2} \vec{r} A \vec{r} + \vec{s} \vec{r} \right) d\vec{r} = \left( \frac{(2\pi)^n}{\det A} \right)^{\frac{1}{2}} \exp\left( \frac{1}{2} \vec{s} A^{-1} \vec{s} \right). \quad (B2)$$

Some useful formulas related to this integral are collected below. By differentiating both sides of the above equation with respect to the $i$th component of the vector $\vec{s}$, $s_i$, we obtain

$$\int r_i \exp\left( -\frac{1}{2} \vec{r} A \vec{r} + \vec{s} \vec{r} \right) d\vec{r} = (A^{-1} \vec{s})_i \left( \frac{(2\pi)^n}{\det A} \right)^{\frac{1}{2}} \exp\left( \frac{1}{2} \vec{s} A^{-1} \vec{s} \right). \quad (B3)$$

Appendix C: Matrix elements of potentials

Analytical integration over $\vec{r}$ in Eq. (12) for certain potentials is possible. These are listed in this Appendix.

1. Gaussian potential

The Gaussian potential operator is given by

$$V(r) = e^{-\mu r^2}. \quad (C1)$$
\[
\langle \Psi_i | V | \Psi_j \rangle = \frac{1}{(\det B)^{1/2}} \langle \Psi_i | \Psi_j \rangle \frac{1}{(\det(B^{-1} + 2\mu I))^{1/2}} \exp \left( -\frac{1}{2} \tilde{b} \tilde{B}^{-1} \tilde{b} + \frac{1}{2} (B^{-1} \tilde{b})(B^{-1} + 2\mu I)^{-1}(B^{-1} \tilde{b}) \right)
\]
\[
= \left( \frac{\det B^{-1}}{\det(B^{-1} + 2\mu I)} \right)^{1/2} \exp \left( -\mu(B^{-1} \tilde{b})(B^{-1} + 2\mu I)^{-1}(B^{-1} \tilde{b}) \right) \langle \Psi_i | \Psi_j \rangle,
\]
(C2)

where substituting \( \mu = 0 \) gives back the overlap matrix as expected.

2. Harmonic oscillator

The harmonic oscillator operator is given by

\( V(r) = \bar{r}^2 \),

(C3)

and its matrix element is given by

\( \langle \Psi_i | V | \Psi_j \rangle = \text{Tr}(B) + \tilde{b}^2 \).

(C4)

---

3. Coulomb Potential

Using the definition

\[
\frac{1}{\bar{r}} = \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-r^2 \rho^2} d\rho,
\]

(C5)

we can evaluate the matrix element of the Coulomb potential

\[
\langle \Psi | \frac{1}{| \bar{r}_i - \bar{r}_j |} | \Psi' \rangle = \frac{2}{\sqrt{\pi}} \int_0^\infty \langle \Psi | e^{-\rho^2(\bar{r}_i - \bar{r}_j)^2} | \Psi' \rangle d\rho
\]

\[
= \frac{2}{\sqrt{\pi}} (2\pi)^{3/2} (\det B)^{1/2} \langle \Psi | \Psi' \rangle \int_0^\infty d\rho \int \exp \left( -\rho^2 \bar{r}^2 - \frac{1}{2}(\bar{r} - \tilde{b}) B^{-1}(\bar{r} - \tilde{b}) \right) d\bar{r}.
\]

(C6)

The integration over \( \bar{r} \) can be done by diagonalizing 3 \( \times \) 3 matrix \( B^{-1} \):

\[
\rho^2 \bar{r}^2 + \frac{1}{2}(\bar{r} - \tilde{b}) B^{-1}(\bar{r} - \tilde{b}) = \sum_{i=1}^3 \left[ \frac{1}{2} \gamma_i + \rho^2 t_i^2 + \mu_i t_i \right] + \frac{1}{2} \tilde{b} B^{-1} \tilde{b},
\]

(C7)

where \( \gamma_i \) is the eigenvalue of \( B^{-1} \) and \( t_i \) is the corresponding eigenvector and \( \mu_i \) is easily determined. Then the integral in Eq. (C6) is

\[
\int \exp \left( -\rho^2 \bar{r}^2 - \frac{1}{2}(\bar{r} - \tilde{b}) B^{-1}(\bar{r} - \tilde{b}) \right) d\bar{r}
\]

\[
= e^{-\frac{1}{2} \tilde{b} B^{-1} \tilde{b}} \prod_{i=1}^3 \int_{-\infty}^{+\infty} \exp \left( -\left( \frac{1}{2} \gamma_i + \rho^2 t_i^2 + \mu_i t_i \right) \right) dt_i = 2^3 e^{-\frac{1}{2} \tilde{b} B^{-1} \tilde{b}} \prod_{i=1}^3 \int_{0}^{+\infty} e^{-\left( \frac{1}{2} \gamma_i + \rho^2 t_i^2 \right)} \cosh(\mu_i t_i) dt_i.
\]

(C8)

We can perform the integration over \( t_i \) and \( \rho \) using

\[
\int_{0}^{+\infty} e^{-a x^2 - \rho^2 x} \cosh(b x) dx = \frac{\sqrt{\pi}}{2a} e^{\frac{\rho^2}{4a}} e^{-\frac{b^2}{4a}}, \quad a > 0,
\]

(C9)

which when used to evaluate Eq. (C8) leads to

\[
\int \exp \left( -\rho^2 \bar{r}^2 - \frac{1}{2}(\bar{r} - \tilde{b}) B^{-1}(\bar{r} - \tilde{b}) \right) d\bar{r} = \pi^2 e^{-\frac{1}{2} \tilde{b} B^{-1} \tilde{b}} \prod_{i=1}^3 (\rho^2 + \frac{1}{2} \gamma_i)^{-\frac{1}{2}} e^{\frac{\mu_i^2}{4(\rho^2 + \gamma_i)}}.
\]

(C10)

By changing \( \rho \) to \( t \) by (see Ref.108)

\[
\rho = \sqrt{a} \frac{t}{\sqrt{1 - t^2}},
\]

(C11)
\[ \rho \text{ integration in Eq. (C6) reduces to a general form} \]
\[ \int_0^\infty \prod_{i=1}^3 (p^2 + a_i) \frac{1}{2} e^{\frac{b_i}{2} + a_i} dp = \sqrt{a} \int_0^1 \prod_{i=1}^3 [a_i + (a - a_i)t^2] \frac{1}{2} e^{\frac{b_i(1-t^2)}{2}} dt. \]  
\[ \text{(C12)} \]

It is clear that the integral reduces to the error function when \( a_i \) is independent of \( i \) and \( a \) is set to that common value of \( a_i \). Even though \( a_i \) differs from each other, by choosing \( a \) equal to, say, the maximum of \( a_1, a_2, a_3 \), the above integrand is a smooth function of \( t \) in \([0, 1]\) and therefore the integral can be accurately evaluated numerically.

---

**Appendix D: Two-particle probability**

We want to calculate the probability of finding a particle in position \( \vec{r} \) and a second one at \( \vec{r}' \) defined as
\[ P(\vec{r}, \vec{r}') = \sum_{i<j} \langle \Psi_i | \delta(\tilde{w}^j - \vec{r})\delta(\tilde{w}^j' - \vec{r}') | \Psi_j \rangle, \]

We define a 3N-dimensional vector \( \vec{K}_j \) as
\[ \vec{k}_j \cdot \tilde{w}^j \vec{r} = \sum_{i=1}^N w_i^j k_i^j \cdot \vec{r}_i = \sum_{i=1}^N w_i^j (k_1^i x_i + k_2^i y_i + k_3^i z_i) = \sum_{i=1}^N w_i^j (k_1^i r_i + k_2^i r_{N+i} + k_3^i r_{2N+i}) \]
\[ = (k_1^j w_i^j, k_2^j w_i^j, k_3^j w_i^j) \vec{r} \equiv \vec{K}_j \vec{r}, \]

where
\[ \vec{K}_j = \begin{pmatrix} k_1^j w_1^j \\ k_2^j w_2^j \\ \vdots \\ k_1^j w_N^j \\ k_2^j w_{N+1}^j \\ \vdots \\ k_2^j w_{2N}^j \\ k_3^j w_{2N+1}^j \\ \vdots \\ k_3^j w_{3N}^j \end{pmatrix}, \]

\[ \text{(D5)} \]

The matrix element, \( \langle \Psi_i | e^{i\vec{K}_j \cdot \vec{r} + i\vec{K}_j \cdot \vec{r}' | \Psi_j \rangle \), is found to be
\[ \langle \Psi_i | e^{i\vec{K}_j \cdot \vec{r} + i\vec{K}_j \cdot \vec{r}' | \Psi_j \rangle = \int e^{-\frac{1}{2} \vec{r} \cdot A \vec{r} + \vec{r} \cdot \vec{K}_j + \vec{r}' \cdot \vec{K}_j} d\vec{r}' = \frac{(2\pi)^{3N}}{(\det A)^{\frac{3N}{2}}} e^{\frac{1}{2} \vec{Q} A^{-1} \vec{Q}}, \]

where \( \vec{Q} \) is 3N-dimensional column vector defined by
\[ \vec{Q} = i\vec{K}_i + i\vec{K}_j + \vec{s} \equiv i\vec{K}_{ij} + \vec{s}, \]

which gives
\[ \vec{Q} A^{-1} \vec{Q} = -\vec{K}_{ij} A^{-1} \vec{K}_{ij} + 2i\vec{s} A^{-1} \vec{K}_{ij} + \vec{s} A^{-1} \vec{s}. \]

\[ \text{(D7)} \]

\[ \text{(D8)} \]
Substituting this result into Eq. (D3) leads to

\[
P(\vec{r}, \vec{r}') = \langle \Psi_i | \Psi_j \rangle \frac{1}{(2\pi)^6} \int \int \exp \left[ -i \vec{k} \cdot \vec{r} - i \vec{k}' \cdot \vec{r}' - \frac{1}{2} K_{ij} A^{-1} \vec{k}_{ij} + i \mathcal{A} A^{-1} \hat{K}_{ij} \right] d\vec{k} d\vec{k}', \tag{D9}
\]

where \( \langle \Psi_i | \Psi_j \rangle \) is given by Eq. (D3). The exponent of the integrand can be expressed as

\[
- i \vec{k} \cdot \vec{r} - i \vec{k}' \cdot \vec{r}' - \frac{1}{2} K_{ij} A^{-1} \vec{k}_{ij} + i \mathcal{A} A^{-1} \hat{K}_{ij}
\]

\[
= - \frac{1}{2} \sum_{\alpha, \beta = 1}^{3} \left( \vec{w}^i A^{-1}_{\alpha \beta} \vec{w}^j k^i_{\beta} + \vec{w}^i A^{-1}_{\alpha \beta} \vec{w}^j k^i_{\beta} + \vec{w}^i A^{-1}_{\alpha \beta} \vec{w}^j k^i_{\beta} + \vec{w}^i A^{-1}_{\alpha \beta} \vec{w}^j k^i_{\beta} \right)
\]

\[
+ i \sum_{\alpha, \beta = 1}^{3} \left( s_{\alpha} A^{-1}_{\alpha \beta} \vec{w}^j k^i_{\beta} + s_{\alpha} A^{-1}_{\alpha \beta} \vec{w}^j k^i_{\beta} - i \sum_{\alpha = 1}^{3} (r_{\alpha} k^i_{\alpha} + r_{\alpha}' k^i_{\alpha}) \right), \tag{D10}
\]

If we define the matrix \( Q \) as a \( 6 \times 6 \) symmetric matrix given by

\[
Q = \begin{pmatrix}
\vec{w}^1 A^{-1}_{11} \vec{w}^1 & \vec{w}^1 A^{-1}_{12} \vec{w}^1 & \vec{w}^1 A^{-1}_{13} \vec{w}^1 & \vec{w}^1 A^{-1}_{14} \vec{w}^1 & \vec{w}^1 A^{-1}_{15} \vec{w}^1 & \vec{w}^1 A^{-1}_{16} \vec{w}^1 \\
\vec{w}^2 A^{-1}_{21} \vec{w}^2 & \vec{w}^2 A^{-1}_{22} \vec{w}^2 & \vec{w}^2 A^{-1}_{23} \vec{w}^2 & \vec{w}^2 A^{-1}_{24} \vec{w}^2 & \vec{w}^2 A^{-1}_{25} \vec{w}^2 & \vec{w}^2 A^{-1}_{26} \vec{w}^2 \\
\vec{w}^3 A^{-1}_{31} \vec{w}^3 & \vec{w}^3 A^{-1}_{32} \vec{w}^3 & \vec{w}^3 A^{-1}_{33} \vec{w}^3 & \vec{w}^3 A^{-1}_{34} \vec{w}^3 & \vec{w}^3 A^{-1}_{35} \vec{w}^3 & \vec{w}^3 A^{-1}_{36} \vec{w}^3 \\
\vec{w}^1 A^{-1}_{41} \vec{w}^1 & \vec{w}^1 A^{-1}_{42} \vec{w}^1 & \vec{w}^1 A^{-1}_{43} \vec{w}^1 & \vec{w}^1 A^{-1}_{44} \vec{w}^1 & \vec{w}^1 A^{-1}_{45} \vec{w}^1 & \vec{w}^1 A^{-1}_{46} \vec{w}^1 \\
\vec{w}^2 A^{-1}_{51} \vec{w}^2 & \vec{w}^2 A^{-1}_{52} \vec{w}^2 & \vec{w}^2 A^{-1}_{53} \vec{w}^2 & \vec{w}^2 A^{-1}_{54} \vec{w}^2 & \vec{w}^2 A^{-1}_{55} \vec{w}^2 & \vec{w}^2 A^{-1}_{56} \vec{w}^2 \\
\vec{w}^3 A^{-1}_{61} \vec{w}^3 & \vec{w}^3 A^{-1}_{62} \vec{w}^3 & \vec{w}^3 A^{-1}_{63} \vec{w}^3 & \vec{w}^3 A^{-1}_{64} \vec{w}^3 & \vec{w}^3 A^{-1}_{65} \vec{w}^3 & \vec{w}^3 A^{-1}_{66} \vec{w}^3 \\
\end{pmatrix}, \tag{D11}
\]

and \( V \) as a 6-dimensional column vector defined by

\[
V = \sum_{\alpha = 1}^{3} \begin{pmatrix}
\vec{w}^1 A^{-1}_{1\alpha} \vec{s}'_{\alpha} \\
\vec{w}^1 A^{-1}_{2\alpha} \vec{s}'_{\alpha} \\
\vec{w}^1 A^{-1}_{3\alpha} \vec{s}'_{\alpha} \\
\vec{w}^1 A^{-1}_{4\alpha} \vec{s}'_{\alpha} \\
\vec{w}^1 A^{-1}_{5\alpha} \vec{s}'_{\alpha} \\
\vec{w}^1 A^{-1}_{6\alpha} \vec{s}'_{\alpha} \\
\end{pmatrix} = \begin{pmatrix}
r_1 \\
r_2 \\
r_3 \\
r_1' \\
r_2' \\
r_3' \\
\end{pmatrix}. \tag{D12}
\]

We can carry out the integration over \( \vec{k}, \vec{k}' \) and express the probability density as

\[
P(\vec{r}, \vec{r}') = \langle \Psi_i | \Psi_j \rangle \frac{1}{(2\pi)^6} \int e^{-\frac{i}{2} Q t + \vec{V} t} dt = \langle \Psi_i | \Psi_j \rangle \frac{1}{(2\pi)^6} \frac{(2\pi)^3}{(\det Q)^{\frac{3}{2}}} e^{-\frac{1}{2} \vec{V} Q^{-1} \vec{V}}. \tag{D13}
\]

To check this expression we integrate it over \( \vec{r}, \vec{r}' \). Defining and the six dimensional column vectors \( \vec{c} \) and \( \vec{\xi} \) as

\[
\vec{c} = \sum_{\alpha = 1}^{3} \begin{pmatrix}
\vec{w}^1 A^{-1}_{1\alpha} \vec{s}'_{\alpha} \\
\vec{w}^1 A^{-1}_{2\alpha} \vec{s}'_{\alpha} \\
\vec{w}^1 A^{-1}_{3\alpha} \vec{s}'_{\alpha} \\
\vec{w}^1 A^{-1}_{4\alpha} \vec{s}'_{\alpha} \\
\vec{w}^1 A^{-1}_{5\alpha} \vec{s}'_{\alpha} \\
\vec{w}^1 A^{-1}_{6\alpha} \vec{s}'_{\alpha} \\
\end{pmatrix}, \tag{D14}
\]

\[
\vec{\xi} = \begin{pmatrix}
r_1 \\
r_2 \\
r_3 \\
r_1' \\
r_2' \\
r_3' \\
\end{pmatrix}, \tag{D15}
\]
we can integrate the probability density over \( r \) and \( r' \) as

\[
\langle \Psi_i \mid \Psi_j \rangle \frac{1}{(2\pi)^6 (\det Q)^{1/2}} \int \int e^{-\frac{1}{2} \tilde{\nu} Q^{-1} \tilde{\nu}} d\tilde{r} d\tilde{r}' = \langle \Psi_i \mid \Psi_j \rangle \frac{1}{(2\pi)^6 (\det Q)^{1/2}} \int \int e^{-\frac{1}{2} \tilde{\xi} \tilde{Q}^{-1} \tilde{\xi}} \tilde{Q}^{-1} \tilde{Q}^{-1} \tilde{\xi} d\tilde{\xi},
\]

where the integral evaluates to

\[
\int e^{-\frac{1}{2} \tilde{\xi} \tilde{Q}^{-1} \tilde{\xi}} \tilde{Q}^{-1} \tilde{Q}^{-1} \tilde{\xi} d\tilde{\xi} = (2\pi)^3 (\det Q)^{-1/2} e^{-\frac{1}{2} \tilde{\xi} \tilde{Q}^{-1} \tilde{\xi}} \tilde{Q}^{-1} \tilde{\xi} = (2\pi)^3 (\det Q)^{-1/2},
\]

and we get back the overlap.

**Appendix E: Generalization of dipole self-interaction**

Eq. (D16) can be generalized straightforwardly to multi-photon modes. By multiplying the kinetic operator with DECG exponential in each photon space, we can remove the quadratic in an analogous way.

\[
-\frac{1}{2} \sum_{n=1}^{N_p} \sum_{i=1}^{3N} \left( \frac{\partial^2}{\partial r_i^2} \right) \exp \left( \alpha_n (\tilde{\lambda}_n \cdot \tilde{D})^2 \right) = -\sum_{n=1}^{N_p} \left( \frac{1}{4\alpha_n} + \frac{1}{2} (\tilde{\lambda}_n \cdot \tilde{D})^2 \right) \exp \left( \alpha_n (\tilde{\lambda}_n \cdot \tilde{D})^2 \right).
\]

where

\[
\alpha_n = \frac{1}{2 \sqrt{\sum_{i=1}^{N} q_i^2 \lambda_n}}
\]

**Acknowledgments**

This work has been supported by the National Science Foundation (NSF) under Grant No. IRES 1826917.

**DATA AVAILABILITY**

Data available on request from the authors.

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