Deformed Explicitly Correlated Gaussians

Honors Thesis

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Abstract

Strong coupling of cavity electromagnetic modes and molecules has emerged as an area of intense theoretical and experimental interest. Such systems are of particular interest due to their ability to modify the physical and chemical properties of materials. In this work, I use a stochastic variational method (SVM) to construct optimized light-matter coupled wave function. By using SVMs to select the best basis states, we are able to achieve highly accurate energies and wave functions. In this work, I will be solving for the Pauli-Fierz (PF) non-relativistic QED Hamiltonian. In this work I will introduce a new basis type Deformed Explicitly Correlated Gaussians (DECGs). DECGs are a modified form of explicitly correlated Gaussians (ECGs) where the basis is chosen such that the dipole self-interaction term can be eliminated. These calculations will be compared to those performed with traditional ECGs, demonstrating their superiority in cases where a non-spherical potential exists, such as the dipole self-interaction term.

Contents

1   Introduction

Few-body systems have reached high accuracy in atomic and molecular systems[6–8;10;14;17;18;24;32–34;42;57;62–64;66;67;76]. Such calculations have proved to be key in explaining a number of properties, including electron correlations[37], relativistic effects[8;13], molecular bonds[12;51;69], and quantum dynamics of the nuclei[9;27;43;68]. One such few-body system of interest is that of small atoms and molecules confined in optical cavities. In recent years, cavity QED has emerged as an area of significant interest for quantum computing. Recently, cavity QED has been proposed as a possibility for realizing a practical quantum computer that avoids the adiabatic condition, while still maintaining robustness[38]. In addition, there has been significant interest in a number of methods of applying cavity QED in the realm of quantum information processing[74].

In addition to applications in quantum computing, cavity QED seems to be particularly useful, and of interest for modifying chemical and physical properties of materials[15;31;50;75]. Applications of this include controlling vibrational energy transfer (VET) in solute molecules[75], excitation transport[19;58], polariton condensation[2;44], transfer of excitation[15], and chemical reactivity[71]. Additionally, theoretical works have explored the use of these systems in excitation and charge transfer[60], self-polarization[26], potential energy surfaces[35], electron transfer[39], and ionization potentials[16].

In a vacuum, high-precision measurements and theoretical calculations have been developed for atoms and molecules, with the accuracy of the theoretical calculation reaching the level of 1 MHz for the dissociation energy of the H_2 molecule[28;49]. However, the same accuracy of theoretical description does not exist for light-matter states. The primary reason for this is that the wave functions for are computationally expensive due to the additional degree of freedom being added, and that methods such as density functional theory (DFT)

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lack suitable functionals for light-matter coupling. In this work, I use stochastic variational calculation (SVM) to construct optimized wave functions for the light-matter coupled system. By selecting the best states, it is possible to achieve highly accurate energies and wave functions. By using stochastic selection, the basis dimension and the computational costs are kept manageable by avoiding high-dimensional tensor product spaces. In this work, I will demonstrate the use of such methods to calculate the behavior of the H_2 groundstate as a function of bond length, and photon coupling strength, energy convergence comparisons for ECG and DECG approaches, and the behavior of H^- ions.

ECGs have been shown to be very useful in cases where the matrix elements are spherically symmetric[10;11;41]. Such systems have been used in a variety of applications, including Efimov physics[5], hyper-fine splitting[46;47], quantum electrodynamic corrections[48], Fermi gasses of cold atoms[77],, and potential energy curves[73]. Despite this success, ECGs are limited in their ability to deal with non-spherical potentials, which make the calculation difficult. Many problems have emerged where non-spherical ECGs are necessary, such as polyatomic molecules or excited states of atoms. One such application where the need for non-spherical ECGs has emerged is in light-matter coupled systems, particularly atoms and molecules in cavity QED[1;20–23;25;26;30;36;52;54;56;59–61;65;70;72]. Such systems are typically described on the level of the Pauli-Fertz (PF) non-relativistic QED Hamiltonian[30;39;56]. Included in this hamiltonian is the dipole self-interaction term $(\vec{\lambda} \cdot \vec{D})^2$, where $\vec{\lambda}$ is the coupling vector of the photons and $\vec{D}$ is the dipole moment of the system. This potential is non-spherically symmetric, making the calculation difficult.

In this work, I will introduce a modified gaussian basis such that the dipole self-interaction term can be removed. The removal of this term makes the remaining calculation much easier due to the restored spherical symmetry. By

doing this, fewer basis are able to be used to reach converged calculations, while maintaining similar levels of accuracy.

2 Formalism

I consider a system of N particles with positions $\vec{r}_1, ... \vec{r}_N$, where $\vec{r}_i = (x_i, y_i, z_i)$, and charges $q_1, ..., q_N$. I define the position vector $\vec{r}$ as follows with x, y and z as our spatial coordinates.

$$\vec{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_N \\ y_1 \\ \vdots \\ y_N \\ z_1 \\ \vdots \\ z_N \end{pmatrix} = \begin{pmatrix} r_1 \\ r_2 \\ \vdots \\ r_N \\ r_{N+1} \\ \vdots \\ r_{2N} \\ r_{2N+1} \\ \vdots \\ r_{3N} \end{pmatrix}. \tag{1}$$

In the following work, $\vec{a}$ will be defined as the 3-dimensional vectors, and a is the single directional vector for a set of particles of the form $\vec{n} = (n_1, \ldots, n_N)$ for some $x, y, z = n$, and $\vec{r}$ is a three dimensional vector formed by a set of single-particle coordinates.

A simple form of DECG functions are defined as

$$\exp\left\{ -\frac{1}{2}\tilde{x}A_{xx}^k x - \frac{1}{2}\tilde{y}A_{yy}^k y - \frac{1}{2}\tilde{z}A_{zz}^k z \right\}$$
$$\times \quad \exp\left\{ -\tilde{x}A_{xy}^k y - \tilde{x}A_{xz}^k z - \tilde{y}A_{yz}^k z \right\}, \tag{2}$$

where $A_{\alpha\beta}$ are $N \times N$ symmetric matrices. With the scalar product $(\tilde{a} \cdot \tilde{b})$ for N-dimensional vectors $\tilde{a} = (a_1, a_2, ..., a_N)$ and $\tilde{b} = (b_1, b_2, ..., b_N)$ is given by $(\tilde{a} \cdot \tilde{b}) = \sum_{m=1}^{N} a_m b_m$. By taking $A_{xx} = A_{yy} = A_{zz} = A$ and $A_{xy} = A_{xz} = $

$A_{yz} = 0$, we get back the original definition of ECGs.

By setting the block matrix A to be defined as

$$A = \begin{pmatrix} A_{xx} & A_{xy} & A_{xz} \\ A_{xy} & A_{yy} & A_{yz} \\ A_{xz} & A_{yz} & A_{zz} \end{pmatrix}, \tag{3}$$

The DECG function can be expressed as

$$\exp\left\{-\frac{1}{2}\vec{r}A^k\vec{r}\right\}, \tag{4}$$

dropping the tilde for simplicity. The superscript k represents the k-th basis function and

$$\vec{r}A^k\vec{r} = \sum_{i,j=1}^{3N} r_i A_{ij}^k r_j. \tag{5}$$

by multiplying the simple DECG by

$$\exp\{\vec{r}\vec{s}\} = \exp\left\{\sum_{i=1}^{3N} s_i r_i\right\}, \tag{6}$$

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

$$\Psi_k = \exp\left\{-\frac{1}{2}\vec{r}A^k\vec{r} + \vec{r}\vec{s}^k\right\}. \tag{7}$$

As an example, take the trial function in the following form

$$\exp\left\{-\frac{1}{2}\sum_{i<j}^{N} \alpha_{ij}^{xx}(x_i - x_j)^2 - \frac{1}{2}\sum_{i<j}^{N} \alpha_{ij}^{yy}(y_i - y_j)^2 - \frac{1}{2}\sum_{i<j}^{N} \alpha_{ij}^{zz}(z_i - z_j)^2\right\} \tag{8}$$

$$\times \exp\left\{-\frac{1}{2}\sum_{i,j=1}^{N} \alpha_{ij}^{xy}(x_i - y_j)^2 - \frac{1}{2}\sum_{i,j=1}^{N} \alpha_{ij}^{xz}(x_i - z_j)^2 - \frac{1}{2}\sum_{i,j=1}^{N} \alpha_{ij}^{yz}(y_i - z_j)^2 - \frac{1}{2}\sum_{i=1}^{N} \beta_i(\vec{r}_i - \vec{c}_i)^2\right\}.$$

In this example, we have a correlation between the particle coordinates and a single particle function centered at $\vec{c}_i$. The relation between the coefficients in Eq. (3) and Eq. (8) is shown in Appendix A of our paper[3].

2.1 Hamiltonian

The description of the Hamiltonian of the system is based on our paper[3] given by

$$H = H_e + H_{ph} = H_e + H_p + H_{ep} + H_d. \tag{9}$$

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. Where the electron-photon interaction is described by using the PF nonrelativistic QED Hamiltonian. The PF Hamiltonian can be derived[39;40;53;56;72] by applying the Power-Zienau-Woolley gauge transformation[45], with a unitary phase transformation on the minimal coupling $(p \cdot A)$ Hamiltonian in the Coulomb gauge

$$H_{ph} = \frac{1}{2} \sum_{\alpha=1}^{N_p} \left[p_\alpha^2 + \omega_\alpha^2 \left(q_\alpha - \frac{\vec{\lambda}_\alpha}{\omega_\alpha} \cdot \vec{D} \right)^2 \right], \tag{10}$$

where $\vec{D}$ is the dipole operator. The photon fields are described by quantized oscillators. $q_\alpha = \frac{1}{\sqrt{2\omega_\alpha}}(\hat{a}_\alpha^+ + \hat{a}_\alpha)$ is the displacement field and p_α is the conjugate momentum. This Hamiltonian describes N_p photon modes with frequency ω_α and coupling $\vec{\lambda}_\alpha$. The coupling term is usually written as[55]

$$\vec{\lambda}_\alpha = \sqrt{4\pi}\, S_\alpha(\vec{r})\vec{e}_\alpha, \tag{11}$$

where $S_\alpha(\vec{r})$ is the mode function at position $\vec{r}$ and $\vec{e}_\alpha$ 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

$$H_p = \sum_{\alpha=1}^{N_p} \left(\frac{1}{2} p_\alpha^2 + \frac{\omega_\alpha^2}{2} q_\alpha^2 \right) = \sum_{\alpha=1}^{N_p} \omega_\alpha \left(\hat{a}_\alpha^+ \hat{a}_\alpha + \frac{1}{2} \right), \qquad (12)$$

and the interaction term is

$$H_{ep} = -\sum_{\alpha=1}^{N_p} \omega_\alpha q_\alpha \vec{\lambda}_\alpha \cdot \vec{D} = -\sum_{\alpha=1}^{N_p} \sqrt{\frac{\omega_\alpha}{2}} (\hat{a}_\alpha + \hat{a}_\alpha^+) \vec{\lambda}_\alpha \cdot \vec{D}. \qquad (13)$$

Only photon states $|n_\alpha\rangle$, $|n_\alpha \pm 1\rangle$ are connected by $\hat{a}_\alpha$ and $\hat{a}_\alpha^+$. The matrix elements of the dipole operator $\vec{D}$ 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

$$H_d = \frac{1}{2} \sum_{\alpha=1}^{N_p} \left(\vec{\lambda}_\alpha \cdot \vec{D} \right)^2. \qquad (14)$$

This term is important for the existence of a ground state as discussed in Ref.[53].

In the following work, it is assumed that there is only one important photon mode with frequency ω and coupling $\vec{\lambda}$. As such, the suffix α has been omitted in what follows. The formalism can be easily extended for many photon modes but this work concentrates on calculating the matrix elements and it is sufficient to use a single-mode.

For one photon mode Eqs. (12) (13) and (14) can be simplified and the Hamiltonian becomes

$$H = T + V + U + \omega \left(\hat{a}^+ \hat{a} + \frac{1}{2} \right) + \omega \vec{\lambda} \cdot \vec{D} q + \frac{1}{2} (\vec{\lambda} \cdot \vec{D})^2, \qquad (15)$$

where T is the kinetic operator

$$T = -\frac{1}{2}\sum_{i=1}^{N}\left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}\right). \tag{16}$$

V is the Coulomb interaction

$$V = \sum_{i<j} V_c(\vec{r}_i - \vec{r}_j), \qquad V_c(\vec{r}_i - \vec{r}_j) = \frac{q_i q_j}{|\vec{r}_i - \vec{r}_j|}. \tag{17}$$

U is an external potential

$$U = \sum_{i=1}^{N} U(\vec{r}_i), \tag{18}$$

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

$$\vec{D} = \sum_{i=1}^{N} q_i \vec{r}_i. \tag{19}$$

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

$$
\begin{aligned}
q|n\rangle &= \frac{1}{\sqrt{2\omega}}\left(a + a^+\right)|n\rangle \tag{20}\\
&= \frac{1}{\sqrt{2\omega}}\left(\sqrt{n}|n-1\rangle + \sqrt{n+1}|n+1\rangle\right).
\end{aligned}
$$

2.2 Dipole self-interaction

The dipole self-interaction can also be readily available using Eq. (58):

$$
\begin{aligned}
\langle\Psi_i|\frac{1}{2}(\vec{\lambda}\cdot\vec{D})^2|\Psi_j\rangle &= \int \frac{1}{2}(\vec{\lambda}\cdot\vec{D})^2 \exp\left\{-\frac{1}{2}\vec{r}A\vec{r} + \vec{r}\vec{s}\right\} d\vec{r} \\
&= \frac{1}{2}\left(\vec{q}A^{-1}\vec{q} + \left(\vec{q}A^{-1}\vec{s}\right)^2\right)\langle\Psi_i|\Psi_j\rangle. \tag{21}
\end{aligned}
$$

2.3 Eliminating the dipole self-interaction

One motivation of DECG is that it is possible to eliminate the dipole self-interaction term of the Hamiltonian. This can be done by selecting a special choice of DECG exponentials. The elimination of this term produces a much simpler Hamiltonian giving a much simpler numerical solution.

The dipole self-interaction term is a special quadratic form and this quadratic form can be represented with a DECG exponent. Using the kinetic energy operator it is possible to find a suitable α to eliminate the dipole self-interaction term:

$$-\frac{1}{2}\sum_{i=1}^{3N}\left(\frac{\partial^2}{\partial r_i^2}\right)\exp\left(\alpha(\vec{\lambda}\cdot\vec{D})^2\right). \tag{22}$$

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

$$\frac{\partial}{\partial x_i}\exp\left(\alpha(\vec{\lambda}\cdot\vec{D})^2\right) = 2\alpha\lambda_1 q_i(\vec{\lambda}\cdot\vec{D})\exp\left(\alpha(\vec{\lambda}\cdot\vec{D})^2\right), \tag{23}$$

and the second derivative

$$\frac{\partial^2}{\partial x_i^2}\exp\left(\alpha(\vec{\lambda}\cdot\vec{D})^2\right) = 2\alpha\lambda_1^2 q_i^2\exp\left(\alpha(\vec{\lambda}\cdot\vec{D})^2\right) \tag{24}$$
$$+ 4\alpha^2\lambda_1^2 q_i^2(\vec{\lambda}\cdot\vec{D})^2\exp\left(\alpha(\vec{\lambda}\cdot\vec{D})^2\right),$$

with similar expressions for y_i and z_i. By choosing α as

$$\alpha = \frac{1}{2\sqrt{\sum_{i=1}^{N}q_i^2}\,\lambda}, \tag{25}$$

where λ is the magnitude of $\vec{\lambda}$, we can express the kinetic energy operator acting

on the exponential as

$$-\frac{1}{2}\sum_{i=1}^{3N}\left(\frac{\partial^2}{\partial r_i^2}\right)\exp\left(\alpha(\vec{\lambda}\cdot\vec{D})^2\right) = -\left(\frac{1}{4\alpha}+\frac{1}{2}(\vec{\lambda}\cdot\vec{D})^2\right)\exp\left(\alpha(\vec{\lambda}\cdot\vec{D})^2\right). \quad (26)$$

This means that by multiplying the basis with the factor

$$\exp\left(\alpha(\vec{\lambda}\cdot\vec{D})^2\right), \quad (27)$$

the dipole self-interaction can be removed and the numerical solution is much simpler. In this way, the nonspherical dipole self-interaction is eliminated, building it into in the basis functions. The generalization of Eq. 26 to multiphoton mode can be found in Appendix E in our paper[3].

3 Results

In this section, I will present the results of a few numerical calculations performed using DECGs as a basis. In this work, the full efficiency of the DECG basis is not explored as the calculations preformed were restricted in the approach to an A matrix of the form

$$A = \begin{pmatrix} A_{xx} & 0 & 0 \\ 0 & A_{xx} & 0 \\ 0 & 0 & A_{xx} \end{pmatrix}, \quad (28)$$

and the trial function is

$$\Psi_k = \exp\left\{-\frac{1}{2}\vec{r}(A^k + 2\alpha(\vec{\lambda}\cdot\vec{D}))\vec{r} + \vec{r}\vec{s}^k\right\}, \quad (29)$$

where α is defined in Eq. (25). Note that if $\alpha = 0$ then this function is the conventional ECG basis function. Nonzero α leads to nonzero off diagonal block

matrices and the basis becomes DECG.

For these calculations, the separable approximation of $1/r$ in terms of Gaussians found here[4] is used

$$\frac{1}{r} = \sum_k w_k \mathrm{e}^{-p_k r^2}.$$ (30)

This approximation allows for the integral in Eqn. (52) to be analytically solved. 89 Gaussian functions with the coefficients w_k and p_k (taken from Ref.[4]) can approximate $1/r$ with an error less than 10^{-8} in the interval $[10^{-9}, 1]$a.u. while using significantly fewer terms than a Gaussian quadrature for comparable accuracy[4].

3.1   2D 2-Electron Harmonic Oscillator

For the first example, I will consider a 2D system of 2 electrons confined to a harmonic oscillator potential, with the potential term given by

$$\frac{1}{2}\omega_0^2 \sum_{i=1}^{2} \vec{r}_i^2,$$ (31)

interacting via a Coulomb potential. This problem is analytically solvable[29] and will be used to compare the ECG ($\alpha = 0$) and DECG solution. By taking $\omega = 0$ in Eq. (15), we ensure that there is no coupling to the photons as the potential is nonspherical because $\lambda \neq 0$. For the test cases, I will use two λ values: $\lambda = 1$ a.u. (the energy is $E = 2.7807764$ a.u.) and $\lambda = 2.5$ ($E = 4.2624689$). Fig. 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
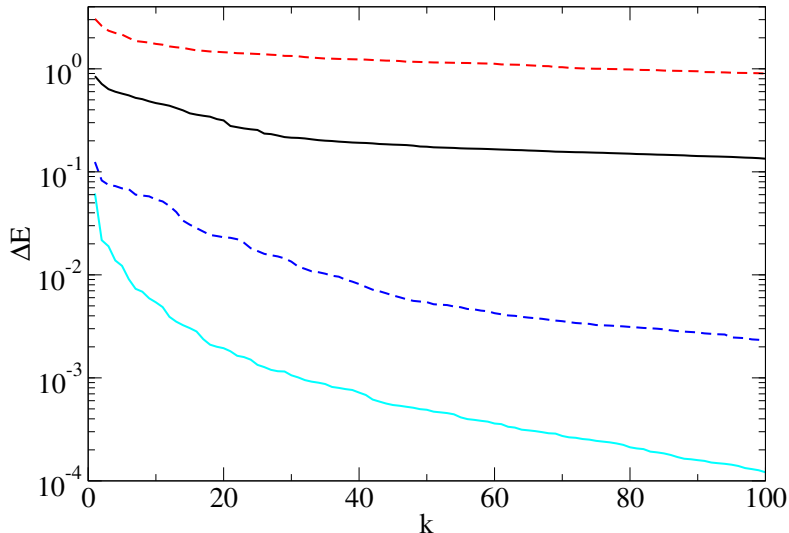
Figure 1: Energy convergence as a function of basis dimension. ΔE is the difference of the calculated energy and the exact energy. The lower two curves are DECG calculations for $\lambda = 1$ a.u. (solid line), $\lambda = 2.5$ a.u. (dashed line); the upper two curves are ECG calculations for $\lambda = 1$ a.u. (solid line), $\lambda = 2.5$ a.u. (dashed line).

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.

3.2 2D H_2 Molecule

The next example is a 2D H_2 molecule with nuclei fixed at distance r. In this case, it is assumed that there is only one relevant photon mode with frequency $\omega = 1.5$ a.u. There are infinitely many photons with energy $n\hbar\omega$ ($n = 0, 1, 2, ...$), but only the lowest photon states are coupled to the electronic part. Eq. (15) is solved using the lowest $n = 0, .., 5$ photon spaces. The energy of a 2D H atom without coupling to the photons is $E = -2$ a.u. When the photons are coupled with $\lambda = 1.5$ a.u. the energy increases to $E = -1.71$ a.u. The increase is largely due to the dipole self-energy part in Eq. (15). The probability amplitudes of
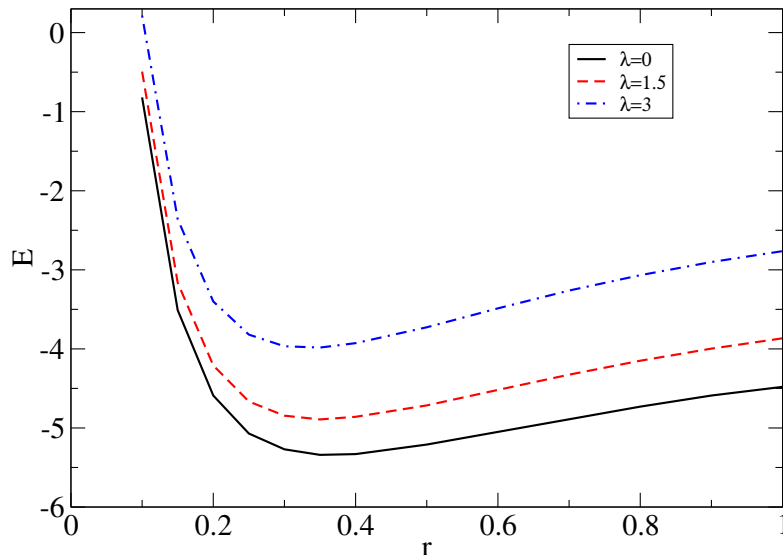
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Figure 2: Energy of the 2D H_2 molecule as a function of the proton-proton distance.

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 however there is a relatively strong coupling between the electrons and light. This is evident by the change in energy between the coupled and uncoupled systems. 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.) suggests a strong coupling strength.

Fig. 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. When the H_2 molecule is coupled to light the energy minimum slightly shifts toward shorter distances. Overall the shape of the three curves is very similar. There is an evident shift upwards as λ increases, which is due to the dipole self-interaction term pushing them higher. The binding energies at

the minimum energy point increase with λ: E_b=1.34 a.u. ($\lambda = 0$), $E_b = 1.47$ ($\lambda = 1.5$ a.u.), and $E_b = 1.68$ a.u. ($\lambda = 3$ a.u.), where E_b is the difference of the energy of the molecule and two times the energy of the H atom.

3.3 H$^-$ ion

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.

In the figure, we see H$^-$ dissociating for strong λ in the finite mass case but remaining stable in the infinite mass case. In the finite mass case, the dissociation happens around $\lambda = 0.08$ 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. (15) 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.
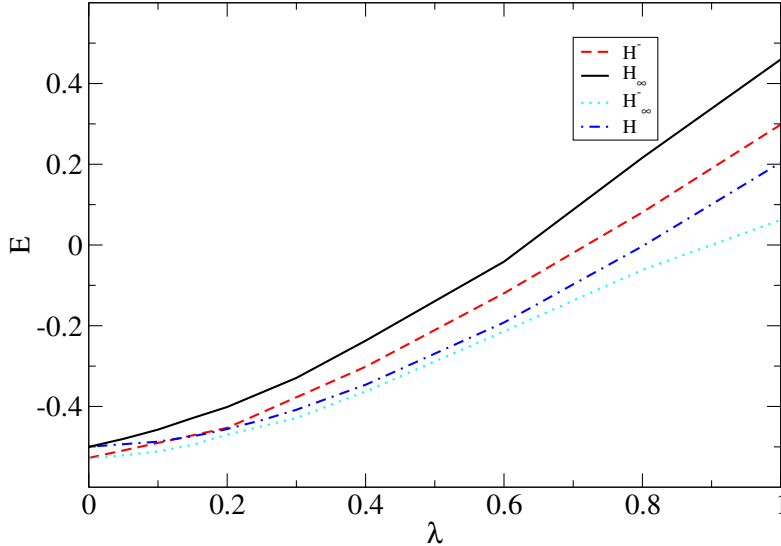

Figure 3: Energy of the 3D H$^-$ ion as a function of λ ($\omega = 0.8$ a.u.

4 Summary

In this work, I have introduced a new variant of ECG basis functions that is suitable for problems involving non-spherical potentials. All necessary matrix elements have been calculated and numerically tested. One issue that arises is that the Coulomb interaction is more complicated than in the conventional ECG case due to the nonspherical integrals that appear in the interaction part Possible solutions to this is are to expand the Coulomb potential in Gaussians allowing for the integration to become analytical, or to use numerical integration.

In this work, it has been shown that using the DECG basis the coupled light-matter equations can be efficiently solved even in cases where the coupling and by extension the dipole self-interaction term is large. This development opens up the possibility to calculate light-matter coupled few-body systems with high accuracy in cavity QED systems.

This approach may be applicable in other cases where there exists a non-spherical potential e.g. calculation of atoms and molecules in magnetic fields.

5 Appendix

5.1 Overlap matrix

The following sections are based on our paper[3]. Additional appendices and more detailed information can be found there. The overlap matrix is given by

$$\langle \Psi_i | \Psi_j \rangle = \int \exp\left\{ -\frac{1}{2}\vec{r}A\vec{r} + \vec{r}\vec{s} \right\} d\vec{r}, \tag{32}$$

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

$$A = A^i + A^j \qquad \vec{s} = \vec{s}^i + \vec{s}^j, \tag{33}$$

and can be calculated using Eq. (56) in Appendix 5.5:

$$\langle \Psi_i | \Psi_j \rangle = \frac{(2\pi)^{3N/2}}{(\det A)^{1/2}} \exp\left\{\frac{1}{2}\vec{s}A^{-1}\vec{s}\right\}. \tag{34}$$

5.2   Kinetic energy

I will express the kinetic energy operator as

$$T = \vec{p}\Lambda\vec{p}, \tag{35}$$

where the momentum operator is given by

$$p_i = -i\hbar\frac{\partial}{\partial r_i} \qquad (i = 1, ..., 3N). \tag{36}$$

For a system of particles with masses $m_1, ..., m_N$, Λ is a block diagonal matrix

$$\Lambda = \begin{pmatrix} \Lambda^x & 0 & 0 \\ 0 & \Lambda^y & 0 \\ 0 & 0 & \Lambda^z \end{pmatrix}, \tag{37}$$

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

$$\Lambda^{\alpha}_{ij} = \frac{1}{2m_i}\delta_{ij}, \tag{38}$$

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

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mass of the nucleus is taken to be infinity). Otherwise. the center of mass motion of the system needs to be removed using

$$\Lambda_{ij}^{\alpha} = \frac{1}{2m_i}\delta_{ij} - \frac{1}{2M},\tag{39}$$

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

Taking the derivative on the right-hand side

$$\frac{\partial}{\partial r_i}\exp\left\{-\frac{1}{2}\vec{r}A^j\vec{r} + \vec{r}\vec{s}\right\} = \left(-(A^j\vec{r})_i + s_i\right)\exp\left\{-\frac{1}{2}\vec{r}A^j\vec{r} + \vec{r}\vec{s}\right\}.\tag{40}$$

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

$$
\begin{aligned}
\langle\Psi_i|T|\Psi_j\rangle &= \int \left(\vec{r}(A^i\Lambda A^j)\vec{r} + \vec{s}^i\Lambda\vec{s}^j - \vec{s}^i\Lambda A^j\vec{r} - A^i\vec{r}\Lambda\vec{s}^j\right)\exp\left\{-\frac{1}{2}\vec{r}A\vec{r} + \vec{r}\vec{s}\right\}d\vec{r}\\
&= \left(\text{Tr}(A^i\Lambda A^k A^{-1}) - \vec{y}\Lambda\vec{y}\right)\langle\Psi_i|\Psi_j\rangle,
\end{aligned}\tag{41}
$$

where we used Eqs. (57) and (58) and define $\vec{y}$ as

$$\vec{y} = A^j A^{-1}\vec{s}^i - A^i A^{-1}\vec{s}^j.\tag{42}$$

5.3   Potential energy

Both V_c and U can be rewritten using a δ function,

$$V_c(\vec{r}_i - \vec{r}_j) = \int \delta(\tilde{w}^{ij}\vec{r} - \vec{r})V_c(\vec{r})d\vec{r},\tag{43}$$

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where $\tilde{w}^{ij}\vec{r}$ is a short-hand notation for $\sum_{k=1}^{N} w_k^{ij}\vec{r}_k$ and in this case we have $w_k^{ij} = \delta_{ik} - \delta_{jk}$. The corresponding formula for U is

$$U(\vec{r}_i) = \int \delta(\tilde{w}^i \vec{r} - \vec{r})U(\vec{r})d\vec{r}, \tag{44}$$

with $w_k^i = \delta_{ik}$. This form allows us to calculate the matrix elements for $\delta(\tilde{w}\vec{r} - \vec{r})$ for a general case without using the particular form of the potential, and to calculate the matrix element of the potential by integration over $\vec{r}$. The δ function can be represented by (dropping the superscript ij and i of w for simplicity)

$$\delta(\tilde{w}\vec{r} - \vec{r}) = \frac{1}{(2\pi)^3} \int e^{i\vec{k}(\tilde{w}\vec{r} - \vec{r})}d\vec{k}. \tag{45}$$

We want to calculate the matrix elements

$$\langle \Psi_i | \delta(\tilde{w}\vec{r} - \vec{r}) | \Psi_j \rangle = \frac{1}{(2\pi)^3} \int\int e^{i\vec{k}(\tilde{w}\vec{r} - \vec{r})} \exp\left\{ -\frac{1}{2}\vec{r}A\vec{r} + \vec{r}\vec{s} \right\} d\vec{r}d\vec{k}. \tag{46}$$

I do this by defining $\vec{t}$ as

$$\vec{t} = \begin{pmatrix} ik_1\tilde{w} \\ ik_2\tilde{w} \\ ik_3\tilde{w} \end{pmatrix} + \vec{s}. \tag{47}$$

Using Eq. (56), the matrix element can be expressed as

$$\begin{aligned}
\langle \Psi_i | \delta(\tilde{w}\vec{r} - \vec{r}) | \Psi_j \rangle &= \frac{1}{(2\pi)^3} \left(\frac{(2\pi)^{3N}}{\det A} \right)^{\frac{1}{2}} \int e^{-i\vec{k}\vec{r}} \exp\left(\frac{1}{2}\vec{t}A^{-1}\vec{t} \right) d\vec{k} \\
&= \frac{1}{(2\pi)^3} \left(\frac{(2\pi)^{3N}}{\det A} \right)^{\frac{1}{2}} \int e^{-i\vec{k}\vec{r}} \exp\left(-\frac{1}{2}\vec{k}B\vec{k} + \frac{1}{2}\vec{s}A^{-1}\vec{s} + i\vec{k}\vec{b} \right) d\vec{k} \tag{48}
\end{aligned}$$

where B is a 3×3 matrix given by

$$
B = \begin{pmatrix} B_{11} & B_{12} & B_{13} \\ B_{12} & B_{22} & B_{23} \\ B_{13} & B_{23} & B_{33} \end{pmatrix}, \tag{49}
$$

with the matrix elements of B defined as

$$
B_{ij} = \sum_{k=(i-1)\cdot N+1}^{i\cdot N} \sum_{l=(j-1)\cdot N+1}^{j\cdot N} w_{k'} A_{kl}^{-1} w_{l'}, \tag{50}
$$

where $k' = k - (i-1) \cdot N$ and $l' = l - (j-1) \cdot N$. And the three dimensional vector $\vec{b}$ is defined as:

$$
b_i = \sum_{k=(i-1)\cdot N+1}^{i\cdot N} w_{k'} \left(A^{-1} \vec{s} \right)_k. \tag{51}
$$

The last integral can again be calculated using Eq. (56) and we have

$$
\langle \Psi_i | \delta(\tilde{w}\vec{r} - \vec{r}) | \Psi_j \rangle = \frac{1}{(2\pi)^{3/2}(\det B)^{1/2}} \exp\left(-\frac{1}{2}(\vec{r} - \vec{b})B^{-1}(\vec{r} - \vec{b}) \right) \langle \Psi_i | \Psi_j \rangle. \tag{52}
$$

Integrating over $\vec{r}$ should give back the overlap, and using Eq. (56) one immediately gets these results.

5.4 Electron-photon coupling

By introducing $\vec{q}$ as

$$
\vec{q} = \begin{pmatrix} \lambda_1 q_1 \\ \lambda_1 q_2 \\ \vdots \\ \lambda_1 q_N \\ \lambda_2 q_1 \\ \vdots \\ \lambda_2 q_N \\ \lambda_3 q_1 \\ \vdots \\ \lambda_3 q_N \end{pmatrix}, \tag{53}
$$

the relevant part of the coupling term can be written as

$$
\vec{\lambda} \cdot \vec{D} = \vec{q}\vec{r}, \tag{54}
$$

and the matrix elements of this term can be easily calculated using Eq. (57)

$$
\begin{aligned}
\langle \Psi_i | \vec{\lambda} \cdot \vec{D} | \Psi_j \rangle &= \int \vec{\lambda} \cdot \vec{D} \exp\left\{ -\frac{1}{2}\vec{r}A\vec{r} + \vec{r}\vec{s} \right\} d\vec{r} \\
&= \vec{q}A^{-1}\vec{s}\, \langle \Psi_i | \Psi_j \rangle.
\end{aligned} \tag{55}
$$

5.5 Generalized Gaussian Integrals

$$
\int \exp\left(-\frac{1}{2}\vec{r}A\vec{r} + \vec{s}\vec{r} \right) d\vec{r} = \left(\frac{(2\pi)^n}{\det A} \right)^{\frac{1}{2}} \exp\left(\frac{1}{2}\vec{s}A^{-1}\vec{s} \right), \tag{56}
$$

By differentiating both sides of the above equation with respect to the ith

component of the vector $\vec{s}$, s_i, we obtain

$$\int r_i \exp\Big(-\frac{1}{2}\vec{r}A\vec{r} + \vec{s}\vec{r}\Big)d\vec{r} \tag{57}$$
$$= (A^{-1}\vec{s})_i \left(\frac{(2\pi)^n}{\det A}\right)^{\frac{1}{2}} \exp\Big(\frac{1}{2}\vec{s}A^{-1}\vec{s}\Big).$$

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

$$\int r_i r_j \exp\Big(-\frac{1}{2}\vec{r}A\vec{r} + \vec{s}\vec{r}\Big)d\vec{r} = \left(\frac{(2\pi)^n}{\det A}\right)^{\frac{1}{2}} \tag{58}$$
$$\times \quad \exp\Big(\frac{1}{2}\vec{s}A^{-1}\vec{s}\Big)\Big\{ (A^{-1})_{ij} + (A^{-1}\vec{s})_i(A^{-1}\vec{s})_j \Big\}$$

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