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Abstract

In order to accurately predict the chemical properties of large molecular systems without drastically increasing the computational cost, one can model electrons as quasi-particles (bare electrons with a screening potential around them). By accounting for this screening in Schrödinger's equation with either a correlation factor of the wave function or an effective Hamiltonian, one can determine a screening parameter for a given system. Then, by optimizing screening parameters for different systems, one can develop a functional relationship for these parameters and use it to improve traditional Hartree-Fock and density functional theory methods to obtain more accurate results, with little increase in computational cost. In the two approaches considered, a variational approach and an effective Hamiltonian approach, there appears to be little correlation between the determined screening parameters from each approach. However, future investigation of the variational and effective Hamiltonian approaches with other correlation factors and other screening potentials, respectively, may produce better results.

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Introduction

Since its early days, quantum mechanics has been used to predict properties of atoms and molecules. One of the major tools to make these predictions is the time-independent Schrödinger's equation (1), a second order partial differential equation that relates the energy, E , of a particle with a wave function ψ through the Hamiltonian operator, \hat{H} .¹

$$\hat{H}\psi = E\psi \tag{1}$$

This equation provides the basis for most modern quantum chemistry and allows one to find the exact energy and wave function of a hydrogen atom, a H_2^+ molecule, and other simple systems. However, systems with more than one electron cannot be solved exactly because of interaction between electrons. Therefore, to obtain the properties of molecular systems, several numerical methods and approximations were developed, such as Hartree-Fock (HF) method, which fails to account for the correlation energy part of the electron-electron interaction.²

Nowadays, a more widely used means of obtaining the properties of molecules is density functional theory (DFT).³ This theory allows one to express the energy in terms of an electron density, rather than a wave function, and often enables one to use less computing power to obtain energies as accurate as many post-HF methods (methods that refine the HF solution to account for the correlation energy). However, even DFT can be very inaccurate for strongly correlated systems, such as transition states of chemical reactions, excited electronic states, and transitional metal complexes.³ By modelling electrons as quasi-particles, particles that consist of a bare point charge and a screening field of opposite sign (Fig. 1),⁴ existing methods such as DFT can be improved to obtain accurate results for strongly correlated systems with little increase in computational cost.

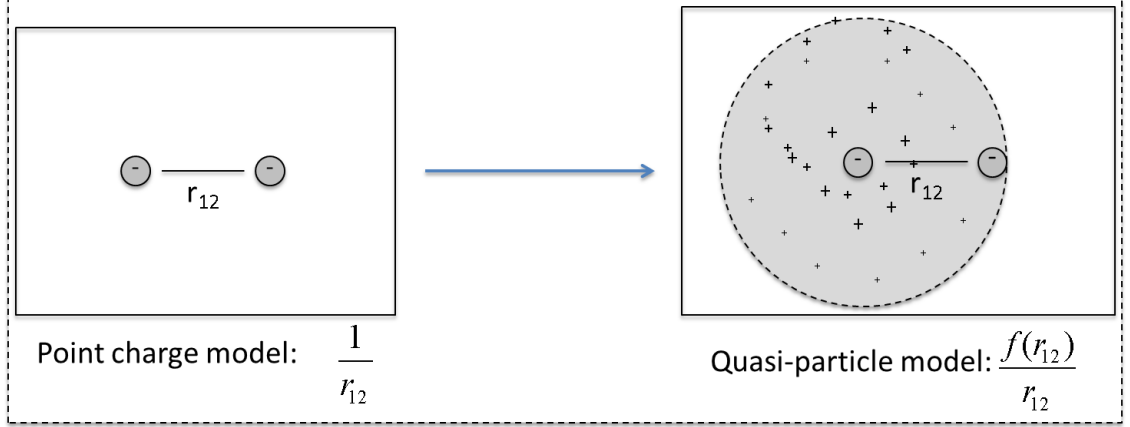


Figure 1: Bare electron-bare electron (left) and quasi-particle-bare electron (right) interaction models

In order to apply the quasi-particle model, one must look at the electron-electron interaction term of the Hamiltonian. For a helium-like ion, our Hamiltonian in atomic units is the following:

$$\hat{H} = \hat{K} + V_{NE} + V_{EE} = \left(-\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} \right) - \left(\frac{z}{r_1} + \frac{z}{r_2} \right) + \left(\frac{1}{r_{12}} \right) \quad (2)$$

where \hat{K} is the kinetic energy operator of the system, V_{NE} is potential energy of nucleus-electron attraction, V_{EE} is the potential energy of electron-electron repulsion, ∇_i^2 is the Laplacian operator for electron i , z is the nuclear charge, and r_{12} is the distance between electrons 1 and 2. Here, the standard electron-electron term, $\frac{1}{r_{12}}$ is an unscreened Coulomb potential. This Coulomb potential can be obtained by solving the Poisson equation:^{1,5}

$$\nabla^2 V_{EE}(\mathbf{r}_{12}) = -4\pi\rho(\mathbf{r}_{12}) \quad (3)$$

where ρ is the charge density. In atomic units, for a simple point charge $\delta(\mathbf{r}_{12})$ with no screening, one has the following:

$$\nabla^2 V_{EE}(\mathbf{r}_{12}) = -4\pi\delta(\mathbf{r}_{12}) \quad (4)$$

Taking the Fourier transform $(\frac{1}{8\pi^3} \int_{\mathbb{R}^3} V_{EE}(r_{12}) e^{-i\mathbf{k}\cdot\mathbf{r}_{12}} d\mathbf{r}_{12})$ of this expression, one obtains:

$$-k^2 U_{EE}(\mathbf{k}) = -\frac{1}{2\pi^2} \quad (5)$$

where U_{EE} is the Fourier transform of V_{EE} . Solving for U_{EE} and taking the inverse Fourier transform $(\int_{\mathbb{R}^3} U_{EE}(k) e^{i\mathbf{k}\cdot\mathbf{r}_{12}} d\mathbf{k})$, one obtains:

$$V_{EE}(\mathbf{r}_{12}) = \frac{1}{r_{12}} \quad (6)$$

The expression above is the electron-electron interaction Coulomb potential of the Hamiltonian. If the particle is screened by a screening function with a charge density of $f(\mathbf{r}_{12})$, the initial equation becomes:

$$\nabla^2 V_{EE}(\mathbf{r}_{12}) = -4\pi(\delta(\mathbf{r}_{12}) - f(\mathbf{r}_{12})) \quad (7)$$

Depending on the charge density of the screening, the solution of this equation can be a Yukawa potential (also called Debye-Huckel and Thomas-Fermi potential), with the equation shown below,^{1,5,6}

$$V_{EE}(\mathbf{r}_{12}) = \frac{e^{-\omega r_{12}}}{r_{12}} \quad (8)$$

where ω is some screening parameter. In addition to a Yukawa screening potential, an Ewald potential, with formula below, can be obtained with a different screening charge density.

$$V_{EE}(\mathbf{r}_{12}) = \frac{erfc(-\omega r_{12})}{r_{12}} \quad (9)$$

Here *erfc* is the complementary error function. All the potential expressions above model the interaction of a quasi-particle with a bare electron. However, a more realistic model is that of the interaction of a quasi-particle with another quasi-particle, as depicted in Figure 2.:

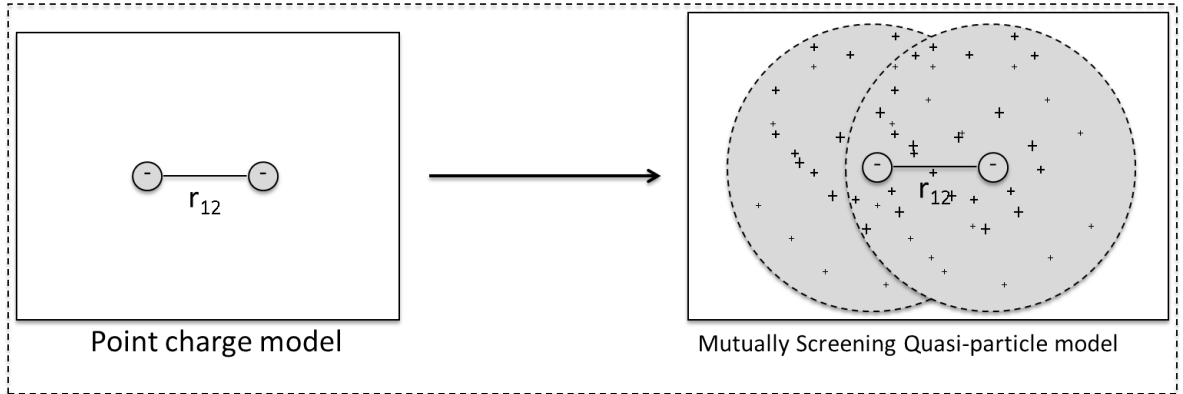


Figure 2: Bare electron-bare electron (left) and quasi-particle-quasi-particle (right) interaction models

The potential expression for varying screening charge densities can be derived by further application of Poisson's equation or through electrostatic analysis. However, such a case was not fully

considered in this research.

By replacing the default term of the Hamiltonian with any of the above screening potentials, one forms the basis for the quasi-particle model for electrons.^{4,7} Figure 3, illustrates the behavior of the different screening potentials. Note that the modified screening potentials decay faster than the Coulomb potential.

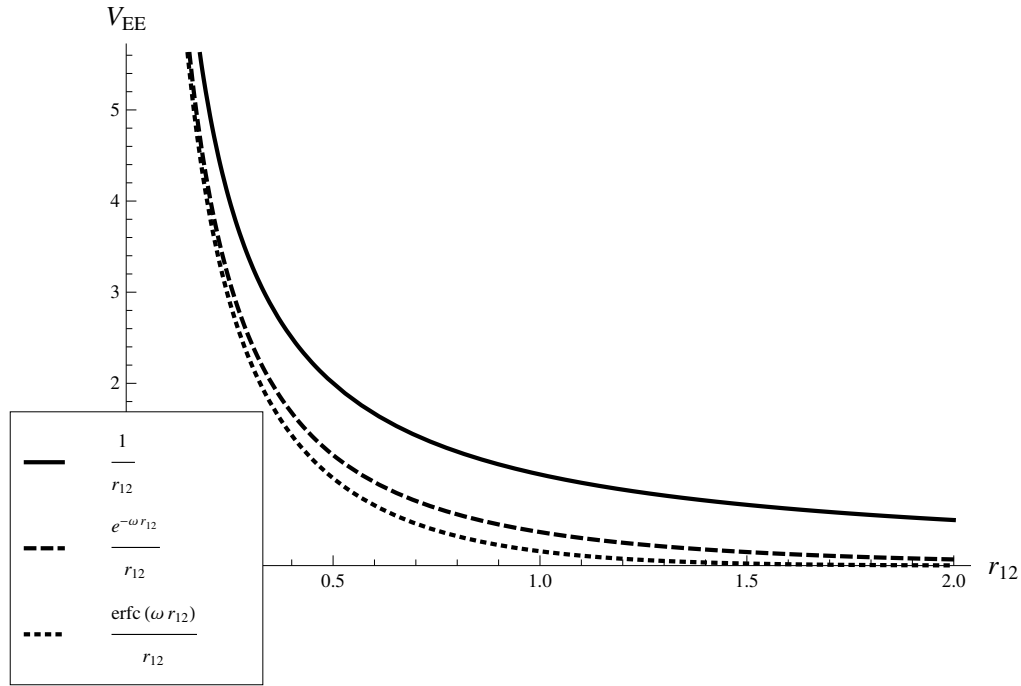


Figure 3: Electron-electron interaction potentials

From here, one can find the expectation value of the energy ($E = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle}$) in terms of ω . However, since the ω parameter appears in the Hamiltonian and not in the wave function, it cannot be determined through energy minimization since no variational principle exists for the Hamiltonian. Instead, one can set the energy expression equal to the "exact" energy (-2.9037 hartree for the He atom²) and solve for ω .

In another approach, one can determine the screening parameter ω by variationally solving Schrödinger's equation using a Hylleraas-type trial wave function.^{8,9} A typical Hylleraas-type wave function for a helium-like ion is:

$$\psi = G(r_{12})\phi_1\phi_2(\alpha_1\beta_2 - \alpha_2\beta_1) \quad (10)$$

where ϕ_i is the atomic orbital of electron i , which is either an exponential or a Gaussian function, $G(r_{12})$ is a correlation factor, and $(\alpha_1\beta_2 - \alpha_2\beta_1)$ is the spin part of the wave function, which cancels out in energy calculations. One of the first correlation factors, originally used by Hylleraas, $G(r_{12}) = r_{12}$, was chosen for its high accuracy around $r_{12} = 0$.⁸ However, due to its inaccurate long-range behavior, Gaussian and exponential correlation factors of the forms $(1 - ce^{-\omega r_{12}^2})$ and $(1 - ce^{-\omega r_{12}})$ have been used, where c is another optimize-able parameter.^{10,11} Compared to the effective Hamiltonian approach, this approach allows one to minimize the energy ($E = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle}$) with respect to the parameter ω using variational methods, because ω is present in the wave function and not in the Hamiltonian. However, this method requires the computation of many complex integrals involving the correlation factor $G(r_{12})$.

By comparing the screening parameter ω from the Hylleraas variational approach with that from the effective Hamiltonian approach, a functional relationship for ω may be established. Then, when the formula for ω is applied to computational methods dealing with large systems, the computational cost is expected to be greatly reduced.

Results

1. Variational Method with Hylleraas-type Wave Functions for the Helium Atom

In this section, the non-modified Hamiltonian from equation 2 is used.

Exponential Orbitals with a Gaussian Correlation Factor. For a Hylleraas wave function, energy expressions were obtained for a wave function with a single exponential orbital per electron and a single Gaussian correlation factor. For this system, the wave function is shown below:

$$\Psi = Ce^{-\alpha(r_1+r_2)} \left(1 - ce^{-\omega r_{12}^2}\right) \quad (11)$$

where α is the orbital exponent (a constant) and C is a normalization constant. The energy calculations were done by approximating exponential orbitals as a sum of Gaussian orbitals, using Eq. 12 and the helium STO-nG (Slater-Type Orbital as n Gaussian Orbitals) coefficients (see Table 2)^{12,13}

with $\alpha = \frac{27}{16}$

$$C e^{-\alpha r} = \sum_{i=1}^n d_i e^{-\xi_i r^2} \quad (12)$$

After obtaining the energy expression, it was minimized with respect to the parameters ω and c . For the STO-1G case, no non-trivial energy minimum was found and the results converged to the Hartree-Fock wave function ($\omega \rightarrow \infty$). This suggests that a single Gaussian orbital was insufficient for this system, and indeed, energies with higher-order Gaussian orbital expansions converged to non-trivial ($\omega < \infty$) minima. All the energies and values of parameters ω and c are enumerated in table 1 below:

Table 1: Optimized parameters for STO-nG orbitals with a Gaussian correlation factor

n	Energy (hartree)	ω	c
1	N/A	N/A	N/A
2	-2.73832	0.6188	0.3049
3	-2.83822	0.6168	0.2832
4	-2.86385	0.6744	0.2691
5	-2.87113	0.6907	0.2648
6	-2.87340	0.6961	0.2634

From these results, the parameter ω appears to converge from below with increasing expansion order of the orbitals, while c appears to converge from above.

Exponential Orbitals with an Exponential Correlation Factor. With the Hylleraas wave functions, an attempt was made to directly obtain the energy expression for a wave function with exponential orbitals and an exponential correlation factor, as shown in the equation below:

$$\psi = C e^{-\alpha(r_1+r_2)} (1 - c e^{-\omega r_{12}}) \quad (13)$$

When calculating the energy, the normalization and potential energy integrals could be evaluated, but the kinetic energy integral could not due to its difficulty. Thus the final energy expression was not obtained through this method.

Instead, both the correlation factors and orbitals were expanded in terms of Gaussian orbitals (see above section) using Eqs. 12 and 14.

$$e^{-\omega r_{12}} = \sum_{i=1}^{ng} d_{g_i} e^{-\xi_{g_i} r_{12}^2} \quad (14)$$

where d_i an ξ_i are the STO-nG constants^{12,13} for the helium atom (Table 2) and d_{g_i} an ξ_{g_i} are the STG-nG (Slater-Type Geminal as n Gaussian Geminals) coefficients (Table 3).¹⁴

Table 2: STO exponents and coefficients for the helium atom

n	ξ	d
1	{0.7739}	$\left(\frac{2\xi}{\pi}\right)^{\frac{3}{4}} \{1.000\}$
2	{2.433, 0.4331}	$\left(\frac{2\xi}{\pi}\right)^{\frac{3}{4}} \{0.4301, 0.6789\}$
3	{6.362, 1.159, 0.3136}	$\left(\frac{2\xi}{\pi}\right)^{\frac{3}{4}} \{0.1543, 0.5353, 0.4446\}$
4	{14.90, 2.726, 0.7574, 0.2514}	$\left(\frac{2\xi}{\pi}\right)^{\frac{3}{4}} \{0.05675, 0.2601, 0.5328, 0.2916\}$
5	{32.29, 5.917, 1.653, 0.5643, 0.2126}	$\left(\frac{2\xi}{\pi}\right)^{\frac{3}{4}} \{0.02214, 0.1135, 0.3318, 0.4826, 0.1936\}$
6	{65.98, 12.10, 3.385, 1.163, 0.4515, 0.1860}	$\left(\frac{2\xi}{\pi}\right)^{\frac{3}{4}} \{0.009164, 0.04936, 0.1685, 0.3706, 0.4165, 0.1303\}$

Table 3: STG exponents and coefficients

ng	ξ_g	d_g
1	$\omega^2 \{0.6853\}$	{0.7354}
2	$\omega^2 \{0.4254, 4.520\}$	{0.5640, 0.3102}
3	$\omega^2 \{0.3303, 2.321, 16.28\}$	{0.4683, 0.3087, 0.1529}
4	$\omega^2 \{0.2783, 1.591, 7.637, 45.74\}$	{0.4025, 0.3090, 0.1570, 0.08898}
5	$\omega^2 \{0.2447, 1.225, 4.924, 19.88, 112.7\}$	{0.3532, 0.3072, 0.1629, 0.09321, 0.05619}
6	$\omega^2 \{0.2209, 1.004, 3.622, 12.16, 45.87, 254.4\}$	{0.3144, 0.3037, 0.1681, 0.09811, 0.06024, 0.03726}

The behaviors of the STO-nG and STG-nG expansions are compared in Figure 4.

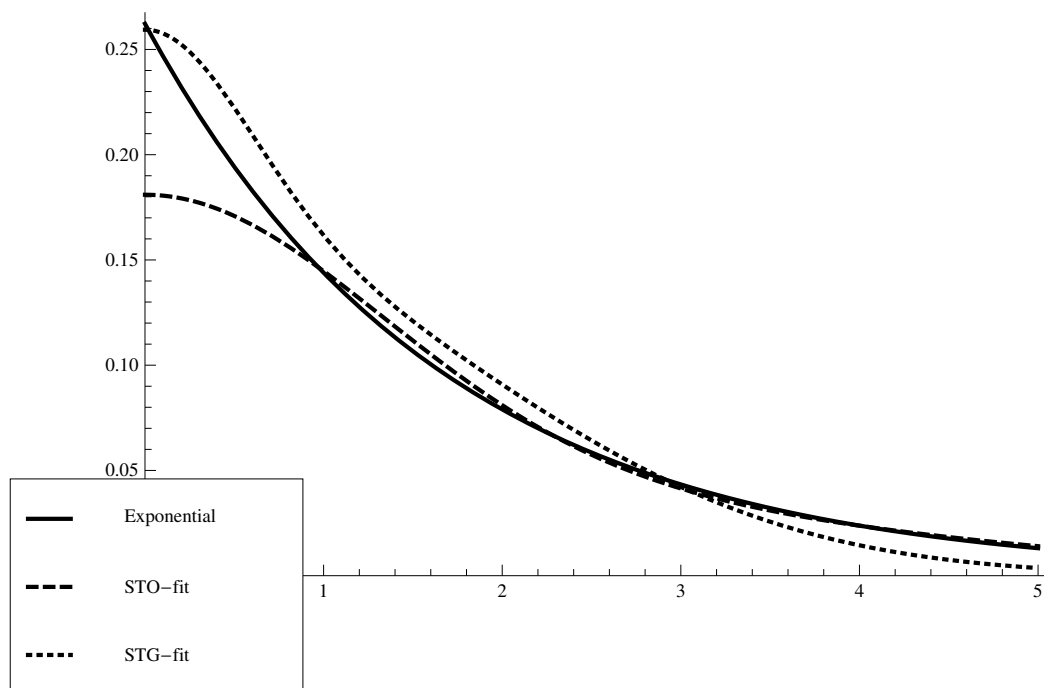


Figure 4: Comparison of STO and STG fits

As shown above, the STG fit is more accurate close to zero, while the STO fit is more accurate further away from zero. Using these expansions, the optimized energy results, values of the coefficient c and values of the screening parameter ω were obtained for each combination of STO and STG coefficients. All these values are presented in Tables 4, 5, and 6, where the bold values represent the most accurate values obtained using the highest expansion orders (STO-6G/STG-6G).

Table 4: Energies calculated with STO-nG orbitals and an STG-nG correlation factor (hartree)

ng	n					
	1	2	3	4	5	6
1	N/A	-2.7383	-2.8382	-2.8638	-2.8711	-2.8734
2	-2.3113	-2.7397	-2.8404	-2.8661	-2.8733	-2.8756
3	-2.3118	-2.7400	-2.8409	-2.8665	-2.8738	-2.8760
4	-2.3125	-2.7402	-2.8411	-2.8667	-2.8739	-2.8762
5	-2.3130	-2.7403	-2.8411	-2.8667	-2.8740	-2.8762
6	-2.3133	-2.7403	-2.8411	-2.8667	-2.8740	-2.8762

Table 5: Values of screening parameter ω , calculated with STO-nG orbitals and an STG-nG correlation factor

ng	n					
	1	2	3	4	5	6
1	N/A	0.9502	0.9487	0.9921	1.0040	1.0078
2	0.7482	0.5236	0.7753	0.7765	0.7919	0.7960
3	0.3653	0.5447	0.5520	0.6100	0.6198	0.6244
4	0.2339	0.4399	0.5138	0.5416	0.5584	0.5629
5	0.1588	0.4176	0.4882	0.5250	0.5382	0.5438
6	0.1121	0.4069	0.4821	0.5189	0.5330	0.5380

Table 6: Values of coefficient c , calculated with STO-nG orbitals and an STG-nG correlation factor

ng	n					
	1	2	3	4	5	6
1	N/A	0.4146	0.3851	0.3659	0.3601	0.3581
2	0.2678	0.4789	0.4089	0.3970	0.3912	0.3893
3	0.3424	0.4648	0.4400	0.4175	0.4118	0.4096
4	0.4208	0.4902	0.4474	0.4296	0.4220	0.4197
5	0.5006	0.4969	0.4534	0.4330	0.4260	0.4234
6	0.5765	0.5004	0.4548	0.4343	0.4270	0.4245

From this data, it can be observed that overall, ω converges from below with higher STO-nG expansion orders, but converges from above with higher STG-nG expansion orders. A similar conclusion holds for coefficient c . When setting the expansion orders equal to each other ($n=ng$), both ω and c remain relatively constant with increasing expansion order and thus it appears that lower orders provide very reasonable initial guesses for the higher orders.

2. Variational Method with Hylleraas-type Wave Functions for He-like Ions

After obtaining the results for the helium atom, further calculations were done for all two-electron ions from H^- to Ne^{8+} with the exponential correlation factor and exponential atomic orbitals. The values of energies and screening parameters using the largest and therefore most accurate expansion (STO-6G/STG-6G) are enumerated in Table 7

Table 7: Exponential correlation factor with exponential orbital values on two-electron ions

Ion	Energy	ω	c
H^-	-0.4972	0.1641	0.7293
He	-2.8762	0.5381	0.4245
Li^+	-7.2513	0.9182	0.2975
Be^{2+}	-13.6249	1.2926	0.2296
B^{3+}	-21.9976	1.6605	0.1876
C^{4+}	-32.3694	2.0204	0.1590
N^{5+}	-44.7404	2.3720	0.1383
O^{6+}	-59.1107	2.7160	0.1227
F^{7+}	-75.4803	3.0523	0.1105
Ne^{8+}	-93.8492	3.3809	0.1007

Here one can see that the optimal ω values tend to increase with higher nuclear charges, while the optimal c values tend to decrease.

3. Effective Hamiltonian Method for the Helium Atom

In this section, the energy expectation integrals were evaluated for different screened potentials in the Hamiltonian, using the given values of the orbital exponent, α . Then, the screening parameter ω was determined using the obtained energy expression. The results from this section are summarized in Table 8

Table 8: Values of the screening parameter ω and orbital exponent α for the helium atom

Screening Potential	Gaussian Orbitals	Exponential Orbitals
Coulomb	$\alpha = \frac{(-1+4\sqrt{2})^2}{9\pi}$	$\alpha = \frac{27}{16}$
Yukawa	$\alpha = \frac{(-1+4\sqrt{2})^2}{9\pi}$ $\omega = 1.0711$	$\alpha = \frac{27}{16}$ $\omega = 0.0582$
Ewald	$\alpha = \frac{(-1+4\sqrt{2})^2}{9\pi}$ $\omega = 0.6740$	$\alpha = \frac{27}{16}$ $\omega = 0.0510^*$

*Obtained via a Gaussian expansion

Gaussian Orbitals with Yukawa Screening. The first screening potential investigated was the Yukawa potential,^{1,5,6} for which energy expressions were obtained for both Gaussian and exponential orbitals. For a single Gaussian orbital, the Hamiltonian and wave function are:

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{z}{r_1} - \frac{z}{r_2} + \frac{e^{-\omega r_{12}}}{r_{12}} \quad (15)$$

$$\Psi = \left(\frac{2\alpha}{\pi}\right)^{3/2} e^{-\alpha(r_1^2+r_2^2)} \quad (16)$$

After transforming the expectation energy expression for this system to Fourier space, simplifying, and transforming back, the following equation was obtained:

$$E = \frac{(2 - 8\sqrt{2})\sqrt{\alpha} + 3\sqrt{\pi}\alpha}{\sqrt{\pi}} - e^{\frac{\omega^2}{4\alpha}} \omega \operatorname{erfc} \left[\frac{\omega}{2\sqrt{\alpha}} \right] \quad (17)$$

Next, the energy was minimized with respect to α for $\omega = 0$. The obtained α of $\frac{(4\sqrt{2}-1)^2}{9\pi}$ was then substituted into (17). Finally, the parameter ω was determined by setting the energy equal to the most accurate literature value of -2.9037 hartree.² For this case, ω was found to be 1.0711. Figures 5, 6, and 7 compare the obtained energies and optimized ω values for different screening potentials and one-electron functions.

Exponential Orbitals with Yukawa Screening: For the Yukawa potential, an energy expression was also obtained when using exponential orbitals. The Hamiltonian and overall wave

function are shown below:

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{z}{r_1} - \frac{z}{r_2} + \frac{e^{-\omega r_{12}}}{r_{12}} \quad (18)$$

$$\psi = \left(\frac{\alpha}{\pi}\right) e^{-\alpha(r_1+r_2)} \quad (19)$$

After calculating the expectation energy integrals, the following energy result was obtained, where $B = 2\alpha + \omega$:

$$E = -4\alpha + \alpha^2 - \frac{68\alpha^5}{B^4} + \frac{38\alpha^4}{B^3} + \frac{\alpha^3}{2B^2} \quad (20)$$

The energy was then minimized with respect to α for $\omega = 0$ to obtain an α of $\frac{27}{16}$. Finally, the parameter ω was determined by setting the energy equal to the most accurate literature value of -2.9037 hartree.² For this case, ω was found to be 0.0582. Figure 5 and 7 compare the obtained energies and their optimized ω values with other screening potentials and orbitals.

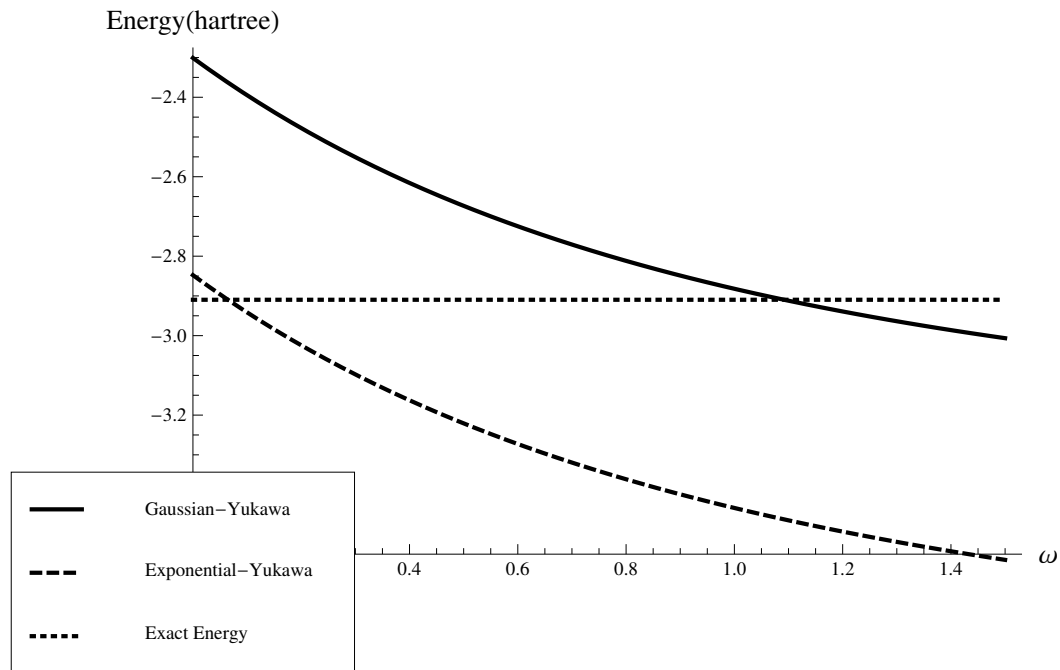


Figure 5: Energy as a function of ω for the Yukawa screening potential with Gaussian and exponential orbitals

Figure 5 compares the energy expressions for a Yukawa screening potential with both Gaussian

and exponential orbitals. One can see that the exponential curve intersects the most accurate energy at a much smaller ω value (0.0582 compared to 1.0711 for Gaussian orbitals). This shows that with the exponential orbitals, much less screening is needed than in the case of Gaussian orbitals. Thus exponential orbitals provide a much more effective basis for wave function, as expected.

Gaussian Orbitals with Ewald Screening. The second potential function investigated was the Ewald potential, for which results for both Gaussian and exponential orbitals were obtained. The Hamiltonian and wave functions used in these calculations are shown below:

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{z}{r_1} - \frac{z}{r_2} + \frac{\text{erfc}(\omega r_{12})}{r_{12}} \quad (21)$$

$$\psi = \left(\frac{2\alpha}{\pi}\right)^{3/2} e^{-\alpha(r_1^2+r_2^2)} \quad (22)$$

After transforming the expectation energy expression for this system to Fourier space, simplifying, and transforming back, the following energy expression was obtained:

$$E = -8\sqrt{\frac{2\alpha}{\pi}} + 3\alpha + \frac{2\left(\sqrt{\alpha} - \frac{\alpha\omega}{\sqrt{\alpha(\alpha+\omega^2)}}\right)}{\sqrt{\pi}} \quad (23)$$

Next, the energy was minimized with respect to α for $\omega = 0$ and obtained an α of $\frac{(4\sqrt{2}-1)^2}{9\pi}$.

Finally, the parameter ω was determined by setting the energy equal to the most accurate literature value of -2.9037 hartree.² For this case, ω was found to be 0.6740. Figures 6, and 7 compare the obtained energies and their optimized ω values with those obtained with the Yukawa potential.

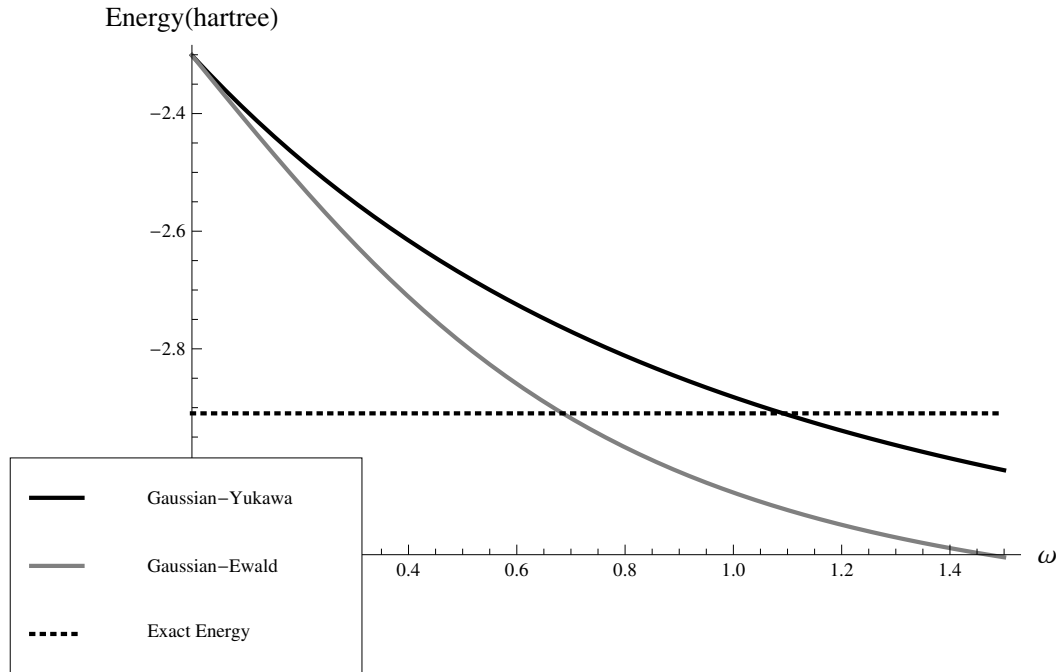


Figure 6: Energy as a function of screening parameter ω for Gaussian orbitals

Figure 6 compares the energy expressions for Gaussian orbitals with both Yukawa and Ewald screening potentials. One can see that the Ewald curve intersects the exact energy at a smaller ω value. This shows that the Ewald screening potential better models the electron-electron screening in a helium atom than the Yukawa potential. Furthermore, this suggests that the Ewald potential is a promising Hamiltonian modification which can potentially be applied to strongly correlated systems.

Exponential Orbitals with Ewald Screening. For the case of an exponential wave function with an Ewald screening potential (Eq. 24), the Hamiltonian and wave function are below:

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{z}{r_1} - \frac{z}{r_2} + \frac{\text{erfc}(\omega r_{12})}{r_{12}} \quad (24)$$

$$\psi = \left(\frac{\alpha}{\pi}\right) e^{-\alpha(r_1+r_2)} \quad (25)$$

The calculations initially could not be done due to the complexity of the electron-electron interaction integral. However, by expanding the exponential orbital in terms of Gaussian orbitals,

by again using the He STO-nG coefficients (Table 2) in a method similar to the Hylleraas case above, energy expressions were obtained. By setting the energy equal to the most accurate literature value of -2.9037 hartree,² ω parameters were obtained. Table 9 summarizes the optimized values of the ω parameter for different expansion orders.

Table 9: Values of screening parameter ω for different expansion orders

n	1	2	3	4	5	6
ω	0.6723	0.1827	0.0854	0.0604	0.0532	0.0510

As expected, the STO-6G expansion has the smallest ω out of all cases in this section, again indicating that Ewald potentials are better models than Yukawa potentials for this system and that exponential orbitals are better atomic models than Gaussian orbitals. Because of this, it is not very surprising that this energy integral required expansion as a sum of Gaussian orbitals to evaluate. All of the results from this section are summarized in the Figure 7 and Table 8 above.

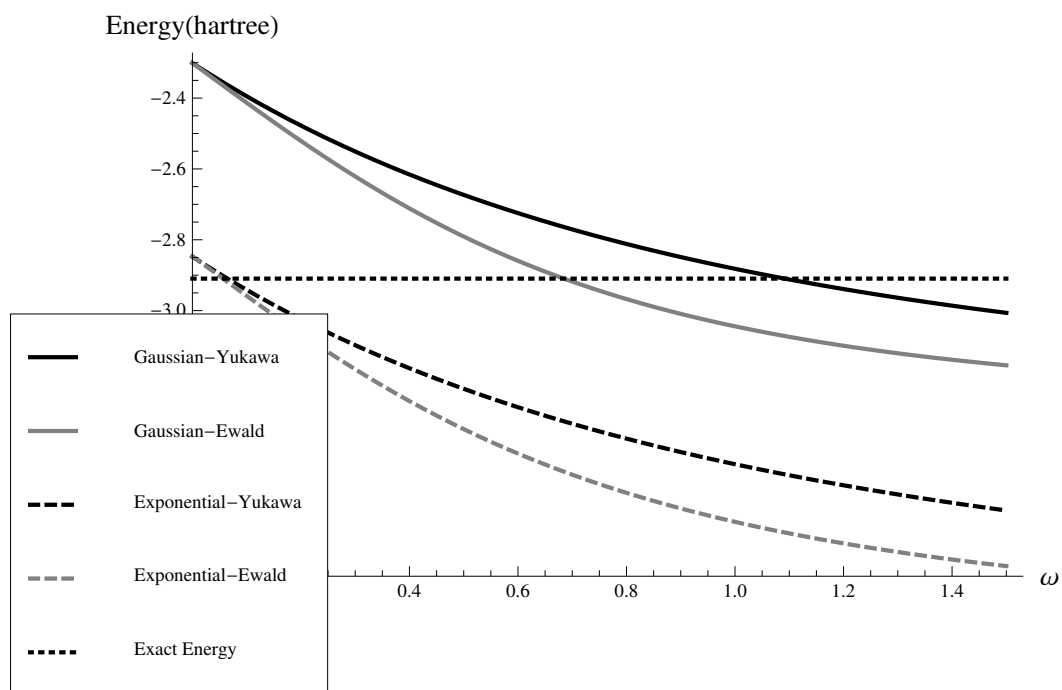


Figure 7: Energy as a function of the screening parameter ω for different orbitals and screening potentials

4. Effective Hamiltonian Method for He-like ions

After performing calculations for the He atom, calculations were done for two-electron He-like ions from H^- to Ne^{8+} . The "exact" energy values used in the calculations are enumerated in the Table 10.

Table 10: Energy values (hartree) used for calculations on two-electron ions

Ion	Exact Energy	Method
H^-	-0.5284	Literature ²
He	-2.9037	Literature ²
Li^+	-7.2622	cc5
Be^{2+}	-13.6359	cc5
B^{3+}	-21.9862	cc5
C^{4+}	-32.3852	cc5
N^{5+}	-44.7608	cc5
O^{6+}	-59.1356	cc5
F^{7+}	-75.5103	cc5
Ne^{8+}	-93.8853	cc5

Note: cc5=CCSD/cc-pV5Z, coupled cluster with singles and doubles using a quintuple-zeta basis set

In addition, for the all the ω calculations in this section, the orbital exponent α for helium-like two-electron ions with Gaussian and exponential orbitals are given by the following formulas, respectively:

$$\alpha = \frac{(2z\sqrt{2} - 1)^2}{9\pi} \quad (26)$$

$$\alpha = z - \frac{5}{16} \quad (27)$$

where z is the atomic number.

Gaussian Orbitals with Yukawa Screening. For the case of Gaussian orbitals with a Yukawa screening potential, the following ω values were obtained (Table 11).

Table 11: Values of ω obtained for two-electron ions with Gaussian orbitals and a Yukawa potential

Ion	H^-	He	Li^+	$Be^{2+}-Ne^{8+}$
ω	0.2509	1.0711	3.7445	DNC

DNC = No feasible solution found ($\omega > 2000$ for all cases)

From these results, one can see that the screening parameter increases with atomic number and that the single Gaussian orbitals are not feasible for higher atomic numbers.

Exponential Orbitals with Yukawa Screening. For the case of exponential orbitals with Yukawa screening, the ω values obtained are summarized in Table 12.

Table 12: Values of ω obtained for two-electron ions with exponential orbitals and a Yukawa potential

Ion	H^-	He	Li^+	Be^{2+}	B^{3+}
ω	0.0613	0.0582	0.0402	0.0387	0.0136

Ion	C^{4+}	N^{5+}	O^{6+}	F^{7+}	Ne^{8+}
ω	0.0379	0.0384	0.0381	0.0378	0.0378

From these results, one can see that ω decreases from H^- to B^{3+} and remains relatively constant from C^{4+} to Ne^{8+} . This suggests that for H^- to B^{3+} , electron-nuclear attraction increases more than electron-electron repulsion with increasing nuclear charge. In contrast, from C^{4+} to Ne^{8+} , the lack of significant change in values of the screening parameter ω suggests that electron-nuclear attraction and electron-electron repulsion increase at about the same rate with increasing nuclear charge.

Gaussian Orbitals with Ewald Screening. For the case of Gaussian orbitals with an Ewald screening potential, the ω values obtained are summarized in Table 13.

Table 13: Values of ω obtained for two-electron ions with Gaussian orbitals and an Ewald potential

Ion	H^-	He	Li^+	$Be^{2+}-Ne^{8+}$
ω	0.1721	0.6740	2.0891	DNC

DNC = No feasible solution found ($\omega > 2000$ for all cases)

As with the Yukawa potential case, one can see that the screening parameter increases with atomic number and that the single Gaussian orbitals are not feasible for higher atomic number. In addition, when comparing the Yukawa and Ewald potential cases, one can see that the same trends for ω hold as for the He atom.

Exponential Orbitals with Ewald Screening. For the case of exponential orbitals with an Ewald screening potential, the ω values obtained are summarized in Table 14

Table 14: Values of ω obtained for two-electron ions with exponential orbitals and an Ewald potential

Ion	H^-	He	Li^+	Be^{2+}	B^{3+}
ω	0.0502	0.0510	0.0378	0.0388	0.0197
Ion	C^{4+}	N^{5+}	O^{6+}	F^{7+}	Ne^{8+}
ω	0.0444	0.0489	0.0534	0.0583	0.0642

Note: All the values in this table were obtained using STO-6G expansions

From these results, one can see that ω decreases from H^- to B^{3+} and increases from C^{4+} to Ne^{8+} . This suggests that for H^- to B^{3+} , electron-nuclear attraction increases more than electron-electron repulsion with increasing nuclear charge. In contrast, from C^{4+} to Ne^{8+} , the increase in values of the screening parameter ω suggests that electron-repulsion increases more than electron-nuclear attraction with increasing nuclear charge. In addition, it appears that the ω values in the Yukawa potential case are actually smaller than in the Ewald case from $Be^{2+}-Ne^{8+}$, contradictory to what was observed in the helium atom case. However, given that all

these results were obtained using Gaussian approximations of exponential orbitals, these results may be influenced slightly by the error in the basis set approximations.

Conclusions

Two methods of accounting for electron-electron screening in helium-like two-electron ions were studied: a variational method with Hylleraas wave functions and an effective Hamiltonian method. For the variational method, energy expressions in terms of ω for Gaussian and exponential orbitals were determined and valuable observations about the behavior of these energy expressions were made. For the effective Hamiltonian method, the energy expressions and ω parameters for different combinations of orbitals and screening potentials were obtained. However, this research still has only scratched the surface of screening functions and developing a functional relationship for ω . Based on these results, there appears to be little correlation in the ω values from each model. However, further investigation of the variational approach with other correlation factors may produce better results. In addition, in the effective Hamiltonian method, the more accurate mutually screening quasi-particle potentials should be further investigated.

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