

Semianalytical wavefunctions and Kohn–Sham exchange-correlation potentials for two-electron atomic systems in two-dimensions

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Abstract

We propose accurate semianalytical wavefunctions for two-electron atomic systems in two-dimensions. These wavefunctions take into account the cusp conditions arising due to the Coulombic nature of external potential and electron–electron interaction, and the screening effects. The first wavefunction is motivated by the Le Sech wavefunction for two-electron atoms and ions in three-dimensions while the second one is constructed to give more variational freedom to the Le Sech wavefunction and is obtained by solving a Schrödinger like equation self-consistently. The results for energies, densities and other quantities are highly accurate and therefore may play an essential role in developing and testing density functional methods for two-dimensional systems.

Keywords: accurate wavefunctions in two-dimensions, two-electron atoms, exchange-correlation potentials in two-dimensions

Kohn–Sham density functional theory [1] is de-facto choice [2] for the study of electronic properties of materials. This is because to get the ground state density of a system it uses only an effective local potential in the Schrödinger-like equation for non-interacting electrons. The potential is the sum of the external potential, Hartree potential and the exchange-correlation (xc) potential $v_{xc} = \frac{\delta E_{xc}[\rho]}{\delta \rho}$. The quantity $E_{xc}[\rho]$ which incorporates many-body effects in it, is known as the exchange-correlation energy functional and needs to be approximated. Over the years many approximate forms of $E_{xc}[\rho]$ have been developed and applied to three-dimensional (3D) systems. However, relatively less attention has been paid to functionals that are tailor-made for two-dimensional (2D) systems. Experimentally these systems can be realized at semiconductor-insulator interfaces [3]. It is naturally expected

and observed that the exchange-correlation functionals developed for 3D systems fail [4–6] to provide accurate physical properties of systems in the pure 2D limit. Thus developing the xc-functionals for 2D system becomes important. Efforts in this direction have been made in the spirit of local density approximation (LDA) [7–9], generalized gradient approximation (GGA) [10–12] and meta-GGA [13–15] approach as used in 3D. To study accuracy of these approximations, it is useful to solve the Schrödinger equation for many-electron 2D systems accurately and then compare results obtained by employing approximate functionals against these.

To test the accuracy of density functionals, wavefunction based studies of atomic systems play an important role. These system are relatively simple to handle computationally and yet capture essential physics of correlation between electrons. They therefore provide fast and reliable resource to test new density functionals for their accuracy. Among these, two-

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electron systems in particular are important because they are the smallest and easiest to deal with computationally. This makes study of two-electron systems in two-dimensions important.

Since the presence of Coulomb interaction between the electrons makes it extremely difficult to solve the corresponding Schrödinger equation, the focus has been on developing approximate but proper forms for the ground state wavefunction. These are then employed to calculate the ground state properties of two-electron systems accurately using the variational method. Ground state wavefunctions developed can be classified into three categories: (i) the ones where the wavefunction has a large number of variational parameters [16–28]; (ii) those where the wavefunction has only a few variational parameters but captures the required physical conditions on it [29–33]; (iii) and finally those where we use basis sets for expanding the wavefunction [34–37].

The present work focuses on developing correlated wavefunctions in two-dimensions for two-electron systems by pursuing approach (ii) mentioned above. Although it is possible to obtain highly accurate numerical solutions [20–28] for two-electron systems, it is nonetheless desirable that simple semianalytical wavefunction also be generated. This is because availability of such wavefunctions greatly facilitates employing them in various applications with ease. For example, if we scale the Coulomb interaction in the Hamiltonian, these wavefunctions may require a simple scaling in their parameters to transform them into the corresponding new wavefunctions [38]. We have employed this scaling in the past to study adiabatic connection in 3D atomic systems [39]. Thus we construct a variational wavefunction for two-electron atomic systems that has only two parameters and satisfies certain properties of the exact wavefunctions. This is motivated from our previous works [38, 40] where we utilized Le Sech wavefunction [30] to develop a semi-analytical wavefunction for three-dimensional systems which gives very accurate energies and densities. As a result, it leads to accurate quantities related to density based theories such as the exchange-correlation potentials [40]. The reason behind such accuracy of the Le Sech wavefunction is commented on after we introduce this wavefunction in the section below.

The two-electron systems we consider in this paper are with two different external potentials. The atomic systems where the external potential has the form $-Z/r$ with Z as the atomic number, and the systems having harmonic-oscillator potential $\frac{1}{2}\omega^2 r^2$ with ω being the frequency as the external potential. The latter are important as the Schrödinger equation for some of these can be solved analytically both in 2D [41, 42] and in 3D [43, 44]. On the other hand while for Coulombic external potential a variety of studies [16–24, 29] have been done for the development of the very accurate form of wavefunctions in three-dimensions, two-electron Coulombic systems in two-dimensions have not received much attention. Some of the works [45, 46] that we are aware of are those where product wavefunction has been used in variational calculations to obtain an analytical expression for the energies of two-electron systems. With these observations it is

evident that further development of more accurate two-electron wavefunctions for two-dimensional system is imperative.

In constructing the wavefunction in the present work one of the main emphasis [30, 40] has been the removal of the effect of poles [47] which arise in the Coulombic external potential and electron–electron interaction potential. Since the physical conditions at the poles in two-dimensions are different from those in three-dimensions, we make the necessary changes in the form of the wavefunction proposed earlier by Le Sech for 3D. We show that the two-dimensional form of this wavefunction is also equally accurate. In particular for harmonic oscillator external potential, where for some values of ω the exact exchange-potential are known, we demonstrate that these wavefunctions give essentially the same results. With the wavefunction proposed, we also calculate exchange-correlation potentials for two-dimensional systems with Coulombic external potential. Accuracy of exchange-correlation potentials for the harmonic oscillator in 2D and 3D and for Coulombic systems in 3D suggests that potentials obtained by us for 2D Coulombic systems will also be highly accurate. Our results indeed demonstrate this and thus provide a benchmark against which potentials calculated from approximate exchange-correlation density functionals for 2D systems can be tested.

We organize the paper into two sections. In the first section, we introduce the Le Sech wavefunction in two-dimensions, and in the subsequent section, we present the modified form of the Le Sech wavefunction. Results for each kind of the wavefunction in the context of density-functional are presented in the corresponding sections. Finally, we conclude the work in the last section.

1. Le Sech wavefunction in two-dimensions

Since the wavefunction we construct is based on 3D Le Sech wavefunction, we have given a comparison of the Hamiltonian, the wavefunction and its properties for 2D and 3D in table 1. We now give the details in following.

The Hamiltonian for two-electron atomic systems in two-dimensions can be written in terms of r_1 , r_2 and $r_{12} = |\vec{r}_1 - \vec{r}_2|$ as (atomic units are used)

$$H = -\frac{1}{2}\nabla_{r_1}^2 - \frac{1}{2}\nabla_{r_2}^2 - \nabla_{r_{12}}^2 - \frac{\vec{r}_1 \cdot \vec{r}_{12}}{r_1 r_{12}} \frac{\partial^2}{\partial r_1 \partial r_{12}} - \frac{\vec{r}_2 \cdot \vec{r}_{12}}{r_2 r_{12}} \frac{\partial^2}{\partial r_2 \partial r_{12}} + v_{ext}(r_1) + v_{ext}(r_2) + \frac{1}{r_{12}}, \quad (1)$$

where Laplacian $\nabla_r^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r}$ and the external potential

$$v_{ext}(r) = \begin{cases} \frac{1}{2}kr^2 & \text{for harmonic potential} \\ -\frac{Z}{r} & \text{for Coulomb potential} \end{cases}. \quad (2)$$

Here $k = m\omega^2$ is the spring constant with frequency ω and Z is the atomic number.

Table 1. In this table, we display the Hamiltonian, wavefunctions proposed, and the various physical conditions to be satisfied by the wavefunctions in two-dimensions and compare them with the corresponding quantities in three-dimensions. Here Z is the atomic number, and a, b are the variational parameters. In 2D Laplacian $\nabla_r^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r}$, and in case of 3D, this is $\nabla_r^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r}$. Atomic units are used throughout.

| | 2D | 3D |
|--|--|--|
| Hamiltonian | $-\frac{1}{2}\nabla_{r_1}^2 - \frac{1}{2}\nabla_{r_2}^2 - \nabla_{r_{12}}^2 - \frac{\vec{r}_1 \cdot \vec{r}_{12}}{r_1 r_{12}} \frac{\partial^2}{\partial r_1 \partial r_{12}} - \frac{\vec{r}_2 \cdot \vec{r}_{12}}{r_2 r_{12}} \frac{\partial^2}{\partial r_2 \partial r_{12}} + v_{ext}(r_1)$ $+ v_{ext}(r_2) + \frac{1}{r_{12}}$ | $-\frac{1}{2}\nabla_{r_1}^2 - \frac{1}{2}\nabla_{r_2}^2 - \nabla_{r_{12}}^2 - \frac{\vec{r}_1 \cdot \vec{r}_{12}}{r_1 r_{12}} \frac{\partial^2}{\partial r_1 \partial r_{12}} - \frac{\vec{r}_2 \cdot \vec{r}_{12}}{r_2 r_{12}} \frac{\partial^2}{\partial r_2 \partial r_{12}} + v_{ext}(r_1)$ $+ v_{ext}(r_2) + \frac{1}{r_{12}}$ |
| Nuclear Cusp condition | $\left. \frac{1}{\Psi} \frac{\partial \Psi}{\partial r} \right _{r=0} = 2Z$ | $\left. \frac{1}{\Psi} \frac{\partial \Psi}{\partial r} \right _{r=0} = Z$ |
| Coulomb cusp condition | $\left. \frac{1}{\Psi} \frac{\partial \Psi}{\partial r_{12}} \right _{r_{12}=0} = 1$ | $\left. \frac{1}{\Psi} \frac{\partial \Psi}{\partial r_{12}} \right _{r_{12}=0} = 0.5$ |
| Le Sech wavefunction | $C_N \exp(-2Zr_1) \exp(-2Zr_2) [\cosh ar_1 + \cosh ar_2]$ $[1 + r_{12} \exp(-br_{12})]$ | $C_N \exp(-Zr_1) \exp(-Zr_2) [\cosh ar_1 + \cosh ar_2]$ $[1 + 0.5r_{12} \exp(-br_{12})]$ |
| $\Psi_L(r_1, r_2 \rightarrow 0, r_{12})$ | $1 - 2Zr_1 - 2Zr_2 + r_{12} + O(r_1^2, r_2^2, r_{12}^2)$ | $1 - Zr_1 - Zr_2 + 0.5r_{12} + O(r_1^2, r_2^2, r_{12}^2)$ |
| $\Psi_L(r_1, r_2, r_{12} \rightarrow 0)$ | $C_N \exp(-2Zr_1) \exp(-2Zr_2) [\cosh ar_1 + \cosh ar_2]$ $[1 + r_{12} + O(r_{12}^2)]$ | $C_N \exp(-Zr_1) \exp(-Zr_2) [\cosh ar_1 + \cosh ar_2]$ $[1 + 0.5r_{12} + O(r_{12}^2)]$ |
| Modified Le Sech wavefunction | $C_N \phi(\vec{r}_1) \phi(\vec{r}_2) [\cosh ar_1 + \cosh ar_2] [1 + r_{12} \exp(-br_{12})]$ | $C_N \phi(\vec{r}_1) \phi(\vec{r}_2) [\cosh ar_1 + \cosh ar_2] [1 + 0.5r_{12} \exp(-br_{12})]$ |

Table 2. We show here the optimizing parameters a , b , total energies E_2 , kinetic energies T , external energy E_{ext} , and the electron–electron interaction V_{ee} calculated for harmonic oscillator potential $0.5\omega^2 r^2$ using Le Sech form of the wavefunction. We also show the electron–electron interaction V_{ee}^{3D} to compare it with the corresponding values in 2D. All the values are in atomic units.

| ω | a | b | E_2 | References E_2 | T | E_{ext} | V_{ee} | V_{ee}^{3D} |
|----------|------|------|--------|------------------|--------|-----------|----------|---------------|
| 0.027 78 | 0.18 | 0.00 | 0.1673 | — | 0.0183 | 0.0622 | 0.0868 | 0.0939 |
| 0.062 50 | 0.21 | 0.00 | 0.3096 | — | 0.0452 | 0.1201 | 0.1443 | 0.1390 |
| 0.166 67 | 0.24 | 0.00 | 0.6716 | 0.6667 [41] | 0.1323 | 0.2730 | 0.2662 | 0.2399 |
| 0.250 00 | 0.24 | 0.00 | 0.9337 | 0.9324 [48] | 0.2057 | 0.3844 | 0.3436 | 0.3028 |
| 0.500 00 | 0.21 | 0.00 | 1.6609 | 1.6598 [49] | 0.4308 | 0.6996 | 0.5305 | 0.4474 |
| 1.000 00 | 0.00 | 0.00 | 2.9998 | 3.0000 [41] | 0.8886 | 1.2954 | 0.8158 | 0.6705 |
| 1.500 00 | 0.10 | 0.05 | 4.2676 | — | 1.3396 | 1.8676 | 1.0605 | 0.8447 |
| 2.000 00 | 0.05 | 0.08 | 5.4962 | — | 1.7979 | 2.4286 | 1.2697 | 0.9874 |
| 2.500 00 | 0.12 | 0.12 | 6.6990 | — | 2.2558 | 2.9826 | 1.4606 | 1.1227 |
| 3.000 00 | 0.12 | 0.15 | 7.8833 | — | 2.7189 | 3.5302 | 1.6341 | 1.2363 |

Note. References E_2 for $\omega = \{0.166\ 67, 1.0\}$ is calculated analytically, and for $\omega = 0.25$ and $\omega = 0.50$ [49] are obtained using configuration interaction and exact diagonalization technique [50], respectively.

Table 3. Shown here are the optimizing parameters a , b , total energies E_2 , kinetic energies T , external energy E_{ext} , and the electron–electron interaction V_{ee} calculated for 2D-He isoelectronic series using Le Sech form of the wavefunction. We also show the electron–electron interaction V_{ee}^{3D} to compare it with the corresponding values in 2D. All the values are in atomic units.

| Z | a | b | E_2 | E_2 [45] | E_2 [46] | T | E_{ext} | V_{ee} | V_{ee}^{3D} |
|-----|------|------|-----------|------------|------------|----------|-----------|----------|---------------|
| 1 | 1.24 | 0.27 | −2.2338 | −1.9960 | −1.9915 | 2.1872 | −5.6020 | 1.1810 | 0.3146 |
| 2 | 1.65 | 0.71 | −11.8881 | −11.6472 | −11.6363 | 11.8904 | −27.2769 | 3.4985 | 0.9487 |
| 3 | 2.00 | 1.17 | −29.5351 | −29.2984 | −29.2811 | 29.5841 | −64.9324 | 5.8132 | 1.5722 |
| 4 | 2.29 | 1.62 | −55.1786 | −54.9496 | −54.9259 | 55.2909 | −118.6063 | 8.1368 | 2.1935 |
| 5 | 2.55 | 2.08 | −88.8202 | −88.6008 | −88.5707 | 89.0003 | −188.2852 | 10.4647 | 2.8181 |
| 6 | 2.79 | 2.55 | −130.4604 | −130.2520 | −130.2155 | 130.7049 | −273.9597 | 12.7944 | 3.4422 |
| 7 | 3.01 | 3.01 | −180.0994 | −179.9032 | −179.8603 | 180.3976 | −375.6208 | 15.1238 | 4.0658 |
| 8 | 3.21 | 3.47 | −237.7373 | −237.5544 | −237.5051 | 238.1209 | −493.3139 | 17.4557 | 4.6904 |
| 9 | 3.40 | 3.93 | −303.3742 | −303.2056 | −303.1499 | 303.8331 | −626.9946 | 19.7873 | 5.3150 |
| 10 | 3.58 | 4.39 | −377.0102 | −376.8568 | −376.7947 | 377.5452 | −776.6745 | 22.1192 | 5.9390 |

The wavefunction we propose for two-electron atomic systems in two-dimensions for harmonic potential is

$$\Psi_L^{2D}(r_1, r_2, r_{12}) = C_N \exp(-0.5\omega r_1^2) \exp(-0.5\omega r_2^2) \times f_1(a, r_1, r_2) f_2(b, r_{12}), \quad (3)$$

while for the Coulomb potential it has the form

$$\Psi_L^{2D}(r_1, r_2, r_{12}) = C_N \exp(-2Zr_1) \exp(-2Zr_2) \times f_1(a, r_1, r_2) f_2(b, r_{12}), \quad (4)$$

where C_N is the normalization constant

$$f_1(a, r_1, r_2) = \cosh ar_1 + \cosh ar_2, \quad (5)$$

$$f_2(b, r_{12}) = 1 + r_{12} \exp(-br_{12}), \quad (6)$$

and a , b are the variational parameters to be optimized. The reason behind taking this form of the wavefunction is: by introducing two kinds of factors and multiplying a product wavefunction (a) takes care of screening of external potential due to electron–electron interaction and (b) satisfies the electron–electron cusp condition arising due to the Coulombic nature of electron–electron interaction. Observe that the logarithmic derivatives of the wavefunction with respect to r and r_{12} in two-dimensions are two times to the corresponding ratio in three-dimensions. Therefore, we replace $\exp(-Zr)$ in three-dimensions by $\exp(-2Zr)$ and $0.5r_{12}$ by r_{12} in f_2 to

construct the wavefunction in two-dimensions. We fix the variational parameters a and b by optimizing the function

$$E_2(a, b) = \langle \Psi_L^{2D} | H | \Psi_L^{2D} \rangle = \int \int \Psi_L^{2D} H \Psi_L^{2D} d\vec{r}_1 d\vec{r}_2 \quad (7)$$

with respect to these parameters.

1.1. Results for the Le Sech wavefunction

We present in tables 2 and 3 the results for the Harmonic oscillator potential for different frequencies and for He-isoelectronic series. To check the accuracy of the wavefunction we also compare the total energies for harmonic oscillator potential with frequencies for which either the analytical or highly accurate numerical results for the energies are available.

Table 2 has the results for the external harmonic potential for various frequencies. As noted above, frequencies $\omega = 0.166\ 67, 0.25, 0.50$ and 1.0 , where the exact results are known our numbers for total energy essentially equal to them. For the parameter a and b , we observe following. Going to the higher frequencies, the behavior of parameter a cannot be predicted. This may be because the structure of the wavefunctions is different for different frequencies. The value of b however increases with frequency and can be understood as a

result of the insignificance of correlation for higher frequencies. Kinetic energy also increases as the systems become more confined for the higher frequencies. As expected, E_{ext} and V_{ee} increase as we go to the higher frequencies. This happens as the strong external potential makes the electron density more compact resulting in the increase in E_{ext} and V_{ee} . Finally, we show the electron–electron interaction V_{ee}^{3D} calculated using the optimized Le Sech form of the wavefunction in three-dimensions. We observe that $V_{ee} > V_{ee}^{3D}$ for all the frequencies except for $\omega = 0.02778$.

Table 3 shows the calculated total energies E_2 , kinetic energies T , electron–nucleus interaction E_{ext} , and the electron–electron interaction V_{ee} along with the optimizing parameters a and b for He-isoelectronic series in two-dimensions. As we go to the larger Z , we observe that the optimizing parameter a increases; this is because for large Z electron density localizes near $r = 0$ resulting in more screening of the nucleus. Parameter b also increases with Z as correlation between electrons becomes relatively less important for larger Z . Comparison of the total energies with those given in [45], that reports a variational calculation with a product wavefunctions, shows that the present results are more negative pointing to the correctness of the wavefunctions. Furthermore, deviations between the two become very small for larger value of Z . It is gratifying to note that the proximity of the total energy to the kinetic energy (satisfaction of the virial relation) i.e. $E_2 \cong -T$. Next, we tabulate the external energy E_{ext} and the inter-electron interaction energy V_{ee} . As we expect, the electron–electron interaction increases for larger values of Z ; this is because the electron density becomes more localized for strong attractive external potential. Finally, we show the electron–electron interaction energy calculated in three-dimensions for the He-isoelectronic series. These energies are calculated using the optimized Le Sech form of the wavefunction in three-dimensions. We observe that V_{ee} in two-dimensions is almost four times that for three-dimensions for a given Z . The main reason for this is that the electrons have to remain in a plane in case of 2D resulting in their being closer to each other in comparison to 3D. We end this section by commenting that the results discussed above show that the proposed variational form for wavefunction captures its correlation nature to a high degree of accuracy. This make it suitable for various studies some of which are reported later in this paper.

2. Modified Le Sech wavefunction in two-dimensions

The second form of the wavefunction we propose is

$$\Psi_{ML}^{2D}(\vec{r}_1, \vec{r}_2) = \phi(r_1)\phi(r_2)f_1(a, r_1, r_2)f_2(b, r_{12}), \quad (8)$$

where the functions f_1 and f_2 are those given in equations (5) and (6), respectively and $\phi(r)$ is a function to be determined. We optimize the energy functional

$$E_2[a, b; \phi] = \langle \Psi_{ML}^{2D} | H | \Psi_{ML}^{2D} \rangle = \int \int \Psi_{ML}^{2D} H \Psi_{ML}^{2D} d\vec{r}_1 d\vec{r}_2 \quad (9)$$

with respect to a , b , and $\phi(r)$ for this purpose. To do this, we

minimize the energy E_2 with respect to $\phi(r)$ for given values of a and b which gives a Schrödinger like equation for $\phi(r)$. The derivation of this equation is similar to that in three-dimensions [38] except that all integrations arising are performed in two-dimensions and the 3D Laplacian is replaced by 2D Laplacian. The steps we follow to calculate ground state energies and the wavefunctions are the following:

1. For given values of a and b , solve the Schrödinger equation (see equation (10) below) self-consistently to get total energies E_2 and $\phi(r)$.
2. Change the values of a and b and again get E_2 and $\phi(r)$ following step 1.
3. Repeat step 2 until we get the minimum energy E_2 and the optimizing function $\phi(r)$.

Next, we provide the details needed for performing the calculation using the modified form of the Le Sech wavefunction in two-dimensions.

2.1. Numerical techniques

The equation we solve for $\phi(r)$ has the following form

$$-\frac{1}{2} \left[\frac{d^2}{dr^2} + \frac{1}{r} \frac{d}{dr} \right] \phi(r) + v_{ext}(r)\phi(r) + v_{eff}(r)\phi(r) = E_2\phi(r), \quad (10)$$

where the expression for the $v_{eff}(r)$ is that given in [38]. Note that the $v_{eff}(r)$ depends on variational parameters a and b . Because of the presence of the first derivative in this equation, we can not use Numerov's method directly in solving this equation. But we do not face this problem on using the logarithmic mesh ($r(x) = e^x$). With this mesh the first derivative is eliminated and the equation becomes

$$-\frac{1}{2} \frac{d^2 \phi(r(x))}{dx^2} + r(x)^2 v_{ext}(r(x)) \phi(r(x)) + r(x)^2 v_{eff}(r(x)) \phi(r(x)) = r(x)^2 E_2 \phi(r(x)). \quad (11)$$

To solve this equation we employ the subroutine written by Paulo [51] for solving the Schrödinger equation. For integration and differentiation arising in the effective potential $v_{eff}(r)$ we employ the subroutines available in the DFTATOM code [52]. The points of the radial grid on logarithmic mesh [53] are given by

$$r_i = r_{min} \left(\frac{r_{max}}{r_{min}} \right)^{\frac{i-1}{N}}, \quad (12)$$

where $r_{min} = \exp(x_{min})/Z$ and $r_{min} = \exp(x_{min})/\omega$ for Coulomb and Harmonic external potentials, respectively with $x_{min} = -12$. We chose $r_{max} = 100/(Z)^{1/3}$ for the Coulomb potential and $r_{max} = 100/(36\omega)^{1/3}$ for the Harmonic potential. Factor 36 is chosen in the latter case to keep $r_{max} = 100$ for the first frequency $\omega = 1/36$. For the accurate calculation the total number of points in the radial grid is taken to be 600. For calculating angular integral 30 points are chosen in the Chebyshev–Gauss method.

Table 4. Optimizing parameters a , b , total energies E_2 , kinetic energies T , external energy E_{ext} , and the electron–electron interaction V_{ee} calculated for harmonic oscillator potential $0.5\omega^2 r^2$ using modified Le Sech form of the wavefunction. All the values are in atomic units.

| ω | a | b | E_2 | T | E_{ext} | V_{ee} |
|----------|------|------|--------|--------|-----------|----------|
| 0.027 78 | 0.14 | 0.00 | 0.1665 | 0.0192 | 0.0626 | 0.0847 |
| 0.062 50 | 0.24 | 0.00 | 0.3087 | 0.0473 | 0.1198 | 0.1417 |
| 0.166 67 | 0.29 | 0.00 | 0.6710 | 0.1356 | 0.2709 | 0.2644 |
| 0.250 00 | 0.32 | 0.00 | 0.9333 | 0.2087 | 0.3829 | 0.3417 |
| 0.500 00 | 0.34 | 0.00 | 1.6608 | 0.4321 | 0.6995 | 0.5291 |
| 1.000 00 | 0.28 | 0.00 | 2.9999 | 0.8877 | 1.2954 | 0.8167 |
| 1.500 00 | 0.23 | 0.05 | 4.2678 | 1.3377 | 1.8676 | 1.0623 |
| 2.000 00 | 0.18 | 0.08 | 5.4964 | 1.7951 | 2.4286 | 1.2724 |
| 2.500 00 | 0.13 | 0.12 | 6.6993 | 2.2529 | 2.9819 | 1.4643 |
| 3.000 00 | 0.08 | 0.15 | 7.8836 | 2.7149 | 3.5300 | 1.6384 |

As the effective potential $v_{eff}(r)$ in equation (10) includes $\phi(r)$, we need to solve the above equation self-consistently. The threshold on the energy is taken to be 10^{-8} to exit the self-consistency cycle and the variational parameters a and b are varied in the interval of 0.01.

2.2. Results for the modified Le Sech wavefunction

In tables 4 and 5, we show the results obtained using the modified Le Sech wavefunction for harmonic potential with different frequencies and for the He-isoelectronic series, respectively. The trends in the values of various quantities for frequency ω and Z is the same as for the Le Sech wavefunction. However, it is to be noticed that the optimizing parameters a and b are different from those obtained for the Le Sech wavefunction. The energies for atomic external potential are consistently lower than Le Sech and for harmonic potential they are either lower than or equal to those obtained from Le Sech wavefunction.

Figures 1 and 2 show orbitals $\phi(r)$, densities $\rho(r)$, and radial densities $r\rho(r)$ for the harmonic and Coulomb potential calculated using the modified form of the wavefunction. Densities and $\phi(r)$ for higher values of ω or Z , are higher at $r = 0$ and decay faster in comparison to the densities and $\phi(r)$ for the lower values of ω or Z .

In the next section we construct the exchange-correlation potentials for the systems being studied and compare with those obtained using approximate exchange-correlation functionals.

3. Exchange-correlation potential for two-electron systems using the LPS equation

To construct the exchange-correlation potential for the wavefunctions obtained, we compare the Levy–Perdew–Sahni (LPS) equation [54]

$$\left[-\frac{1}{2}\nabla^2 + v_{ext}(\vec{r}) + v_{eff}^{LPS}(\vec{r})\right]\rho^{1/2}(\vec{r}) = \mu\rho^{1/2}(\vec{r}), \quad (13)$$

with the Kohn–Sham equation for two-electron systems

$$\left[-\frac{1}{2}\nabla^2 + v_{ext}(\vec{r}) + v_H(\vec{r}) + v_{xc}(\vec{r})\right]\rho^{1/2}(\vec{r}) = \epsilon\rho^{1/2}(\vec{r}) \quad (14)$$

which gives

$$v_{xc}(\vec{r}) = v_{eff}^{LPS}(\vec{r}) - v_H(\vec{r}). \quad (15)$$

Here $v_H(\vec{r}) = \int \frac{\rho(\vec{r}_2)}{|\vec{r} - \vec{r}_2|} d\vec{r}_2$ is the Hartree potential. LPS expressed the $v_{eff}^{LPS}(\vec{r})$ in terms of ground state wavefunction. For two-electron atomic systems, this is

$$\begin{aligned} v_{eff}^{LPS}(\vec{r}_2) = & \int \frac{\tilde{\rho}_1(\vec{r}_1; \vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 \\ & + \left\langle \phi_1 \left| -\frac{1}{2}\nabla_1^2 + v_{ext}(r_1) - E_1 \right| \phi_1 \right\rangle \\ & + \frac{1}{2} \int |\tilde{\nabla}_2 \tilde{\rho}_1(\vec{r}_1; \vec{r}_2)|^2 d\vec{r}_1, \end{aligned} \quad (16)$$

where

$$\begin{aligned} \phi_1(\vec{r}_1; \vec{r}_2) = & \sqrt{\frac{2}{\rho(\vec{r}_2)}} \Psi_2(\vec{r}_1, \vec{r}_2), \\ \rho(\vec{r}_2) = & 2 \int |\Psi_2(\vec{r}_1, \vec{r}_2)|^2 d\vec{r}_1 \end{aligned} \quad (17)$$

and

$$\tilde{\rho}_1(\vec{r}_1; \vec{r}_2) = |\phi_1(\vec{r}_1; \vec{r}_2)|^2.$$

The integrals arising here are performed in 2D space. We employ the LPS approach because it has been observed that LPS effective potential leads to accurate exchange-correlation potentials.

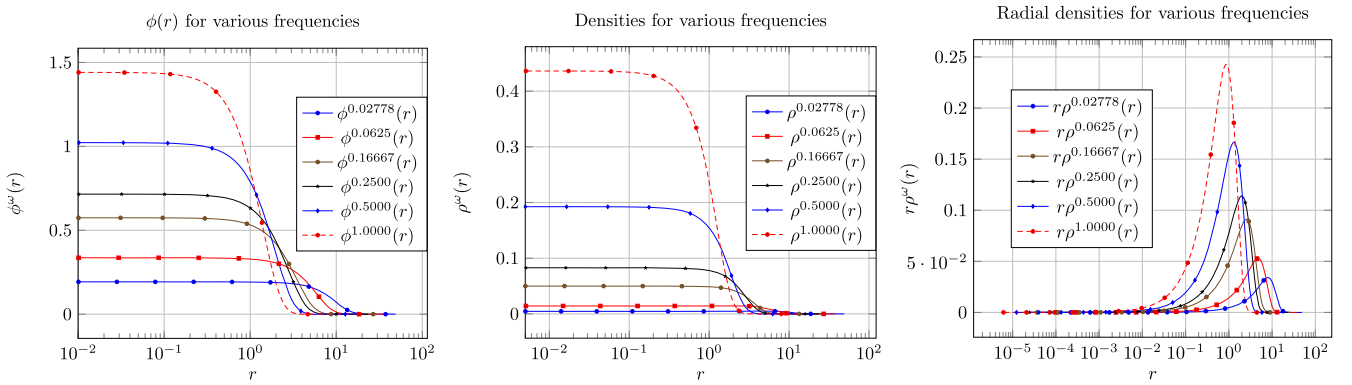
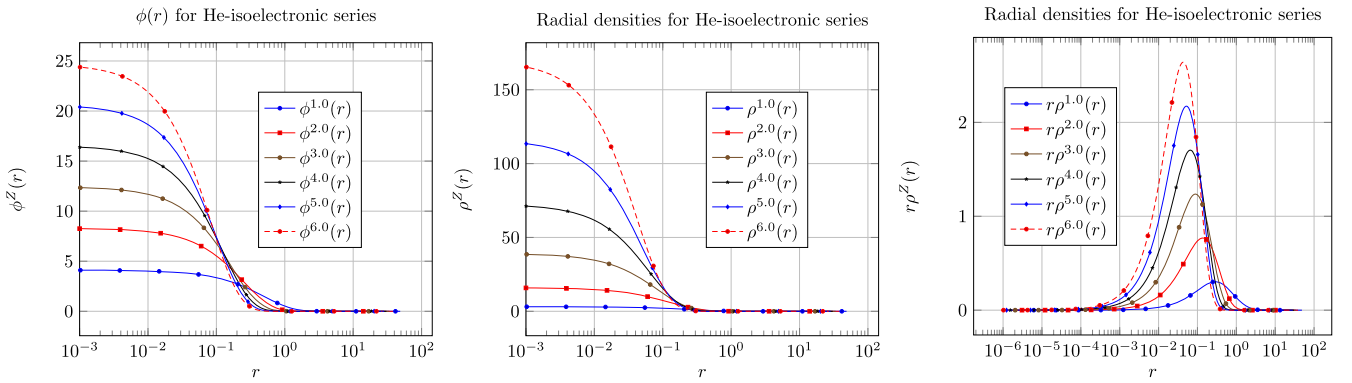
To calculate $v_{xc}(\vec{r})$, we first obtain $v_{eff}^{LPS}(\vec{r})$ for the Le Sech form of the wavefunction and then the exchange-correlation potential using equation (15). To establish accuracy of $v_{xc}(\vec{r})$, in figure 3(a) we compare $v_{xc}(\vec{r})$ for $\omega = 1$ calculated from the Le Sech wavefunction with the exact exchange-correlation potential for this system obtained by inverting the analytical expression for the exact density [41, 42]. It is evident from the figure that $v_{xc}(\vec{r})$ obtained by us is nearly the same as the exact exchange-correlation potential.

Having shown that for $\omega = 1$ the potential obtained by us is almost exact, we next calculate it for other frequencies and for the He-isoelectronic series. These are shown in figure 4. Our experience of calculating xc-potential this way and other work [56] in the literature for the three-dimensional systems shows that the xc-potential calculated using LPS equation comes out to be highly accurate. Therefore, we expect that our results in figure 4 represent the corresponding exchange-correlation potential very accurately. As such these will be useful for comparison purpose in density functional studies in two-dimensions. We do it next for two functionals available in 2D.

In figure 3, we compare the exchange-correlation potential for the harmonic potential ($\omega = 1$) and atom ($Z = 6$) with exchange-correlation potential for the LDA (exchange-

Table 5. Optimizing parameters a , b , total energies E_2 , kinetic energies T , external energy E_{ext} , and the electron–electron interaction V_{ee} calculated for 2D-He isoelectronic series using modified Le Sech form of the wavefunction. All the values are in atomic units.

| Z | a | b | E_2 | T | E_{ext} | V_{ee} |
|-----|------|------|-----------|----------|-----------|----------|
| 1 | 1.41 | 0.28 | −2.2359 | 2.2412 | −5.6555 | 1.1792 |
| 2 | 2.22 | 0.76 | −11.8924 | 11.9270 | −27.3018 | 3.4839 |
| 3 | 2.90 | 1.25 | −29.5399 | 29.6021 | −64.9365 | 5.7972 |
| 4 | 3.51 | 1.75 | −55.1836 | 55.2734 | −118.5730 | 8.1205 |
| 5 | 4.07 | 2.25 | −88.8253 | 88.9432 | −188.2094 | 10.4477 |
| 6 | 4.59 | 2.75 | −130.4655 | 130.6123 | −273.8452 | 12.7770 |
| 7 | 5.06 | 3.24 | −180.1044 | 180.2808 | −375.4798 | 15.1072 |
| 8 | 5.51 | 3.74 | −237.7423 | 237.9492 | −493.1139 | 17.4386 |
| 9 | 5.92 | 4.23 | −303.3792 | 303.6176 | −626.7467 | 19.7703 |
| 10 | 6.31 | 4.72 | −377.0151 | 377.2860 | −776.3785 | 22.1023 |

**Figure 1.** We display here the calculated function $\phi^\omega(r)$, densities $\rho^\omega(r)$, and the corresponding radial densities $r\rho^\omega(r)$ for various frequencies ω using the modified form of Le Sech wavefunction. The logarithmic x axis is being used for the plotting.**Figure 2.** Displayed here are the calculated function $\phi^Z(r)$, densities $\rho^Z(r)$, and the corresponding radial densities $r\rho^Z(r)$ for various values of Z using the modified form of Le Sech wavefunction. The logarithmic x axis is being used for the plotting.

functional [11] $\left(-\frac{8}{3\sqrt{\pi}2^{3/2}}\int\rho^{3/2}(\vec{r})d\vec{r}\right)$ combined with AMGB [9] or PRM [55] correlation-functionals). We use the LIBXC library [57] for calculating these potentials. We observe that the LDA exchange-correlation potentials calculated for the Le Sech density for $\omega = 1$ deviates from the exact exchange-correlation potential and underestimates its magnitude. Furthermore, it decays faster than the exact potential asymptotically. In figure 3(b), we show the LDA $v_{xc}(\vec{r})$ and the accurate $v_{xc}(\vec{r})$ obtained for the He-like atom ($Z = 6$). Here also the LDA exchange-correlation potential shows the same behavior as for the harmonic potential

systems. The difference between AMGB and PRM functional at the first grid point is 0.07 a.u. while the deviation of these at the same point from the present xc-potential is around 2 a.u.

Finally, to test the accuracy of xc-functionals we compare the chemical potential calculated using equation (13) with that obtained using the expression $\mu = E_2 - E_1$ in tables 6 and 7 for harmonic oscillator and Coulomb potential, respectively. For harmonic potential $E_1 = \omega$ and for Coulomb potential this is equal to $-2Z^2$. Ideally two values of chemical potentials should be equal [58] to each other, and equal to the eigenvalue of highest occupied orbital in DFT calculation.

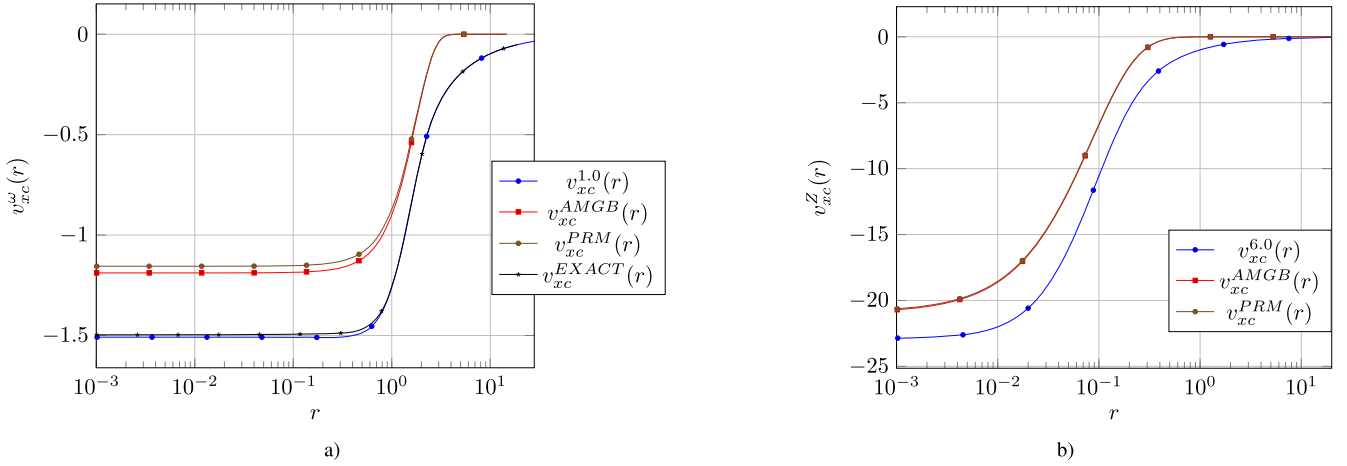


Figure 3. In the left plot (a) we compare the exchange-correlation potentials $v_{xc}^1(\vec{r})$ for harmonic oscillator potential with $\omega = 1$ with the exact exchange-correlation potential obtained from its exact density [41, 42]. We also plot the potential within the LDA (exchange-functional [11] $\left(-\frac{8}{3\sqrt{\pi}2^{3/2}} \int \rho^{3/2}(\vec{r}) d\vec{r}\right)$ combined with AMGB [9] or PRM [55] correlation-functionals). In the right plot (b) we show the exchange-correlation potential for the Coulomb external potential for $Z = 6$ and compare it with the corresponding exchange-correlation potentials obtained for the functionals mentioned above.

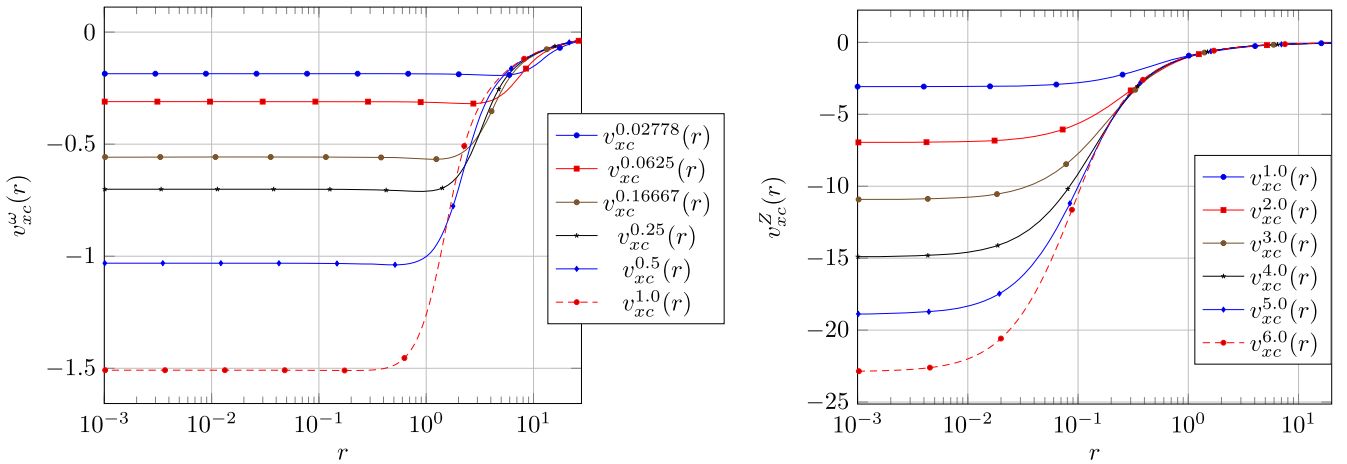


Figure 4. Exchange-correlation potentials $v_{xc}^\omega(\vec{r})$ for harmonic oscillator potential with different frequencies and $v_{xc}^Z(\vec{r})$ for He-isoelectronic series

The results shown in the tables satisfy this condition very well. In addition, we also show the eigenvalues of highest occupied orbital in density functional calculations using PRM and AMGB correlation functional with the above mentioned LDA exchange functional. The eigenvalues obtained from PRM and AMGB functionals deviate from the present results. This is because the LDA is expected to work better for the homogeneous systems. It can be seen when ω gets smaller the eigenvalues obtained from PRM and AMGB come closer to the μ or $E_2 - E_1$. In case of Coulomb potential it does behave in the similar way due to the form of the potential which does not get flat even for the small value of Z as happens in case of harmonic potential for small ω .

4. Concluding remarks

Two-electron systems are the simplest correlated systems and can provide insights into understanding the physics behind the correlation effects arising due to the Coulomb interaction between electrons. In addition to this, it is also interesting to study these systems in the reduced dimensional space as such systems are also getting both experimental and theoretical attention.

The above mentioned reasons make this work significant as we propose two accurate forms of the wavefunctions for two-electron systems in two-dimensions. This was motivated by our study in three-dimensions that showed that these forms of the wavefunction provides accurate densities as well as energies for these systems. Therefore, we expect that the present wavefunction to play an important role in understanding the systems in two-dimensions and in studying other aspects in electronic structure calculations.

Table 6. Chemical potential μ calculated using equation (13), the difference $E_2 - E_1$ with $E_1 = \omega$, and the highest occupied orbital eigenvalues in Kohn–Sham equation using AMGB and PRM correlation functionals with LDA exchange functional for Harmonic oscillator potential as the external potential.

| ω | Le Sech | | Modified Le Sech | | PRM | AMGB |
|----------|---------|-------------|------------------|-------------|--------|--------|
| | μ | $E_2 - E_1$ | μ | $E_2 - E_1$ | | |
| 0.027 78 | 0.1387 | 0.1395 | 0.1384 | 0.1387 | 0.1697 | 0.1674 |
| 0.062 50 | 0.2460 | 0.2471 | 0.2455 | 0.2462 | 0.3040 | 0.3004 |
| 0.166 67 | 0.5025 | 0.5049 | 0.5021 | 0.5043 | 0.6198 | 0.6122 |
| 0.250 00 | 0.6802 | 0.6837 | 0.6799 | 0.6833 | 0.8342 | 0.8240 |
| 0.500 00 | 1.1545 | 1.1609 | 1.1544 | 1.1608 | 1.3919 | 1.3770 |
| 1.000 00 | 1.9884 | 1.9998 | 1.9884 | 1.9999 | 2.3459 | 2.3232 |
| 1.500 00 | 2.7542 | 2.7676 | 2.7542 | 2.7678 | 3.2003 | 3.1733 |
| 2.000 00 | 3.4807 | 3.4962 | 3.4807 | 3.4964 | 4.0016 | 3.9716 |
| 2.500 00 | 4.1823 | 4.1990 | 4.1823 | 4.1993 | 4.7683 | 4.7360 |
| 3.000 00 | 4.8652 | 4.8833 | 4.8652 | 4.8836 | 5.5103 | 5.4760 |

Table 7. Chemical potential μ calculated using equation (13), the difference $E_2 - E_1$ with $E_1 = -2Z^2$, and the highest occupied orbital eigenvalues in Kohn–Sham equation using AMGB and PRM correlation functionals with LDA exchange functional for Coulomb external potential.

| Z | Le Sech | | Modified Le Sech | | PRM | AMGB |
|-----|-----------|-------------|------------------|-------------|-----------|-----------|
| | μ | $E_2 - E_1$ | μ | $E_2 - E_1$ | | |
| 1 | −0.2371 | −0.2338 | −0.2243 | −0.2359 | −0.0370 | −0.0525 |
| 2 | −3.9091 | −3.8880 | −3.8484 | −3.8924 | −3.1641 | −3.2038 |
| 3 | −11.5698 | −11.5350 | −11.4659 | −11.5399 | −10.2891 | −10.3382 |
| 4 | −23.2264 | −23.1784 | −23.0801 | −23.1836 | −21.4130 | −21.4674 |
| 5 | −38.8809 | −38.8198 | −38.6934 | −38.8253 | −36.5365 | −36.5943 |
| 6 | −58.5338 | −58.4598 | −58.3074 | −58.4655 | −55.6597 | −55.7199 |
| 7 | −82.1858 | −82.0985 | −81.9280 | −82.1044 | −78.7826 | −78.8446 |
| 8 | −109.8368 | −109.7361 | −109.5481 | −109.7423 | −105.9053 | −105.9687 |
| 9 | −141.4869 | −141.3727 | −141.1746 | −141.3792 | −137.0277 | −137.0923 |
| 10 | −177.1362 | −177.0081 | −176.8023 | −177.0151 | −172.1500 | −172.2155 |

We have calculated total, kinetic, electron-nucleus interaction and the inter-electron interaction energies for these systems using both forms of the wavefunction. We have also compared the exchange-correlation potential obtained by us with the corresponding LDA exchange-correlation potential and shown the difference between them.

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References

- [1] Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133
- [2] Pribram-Jones A, Gross D A and Burke K 2015 *Annu. Rev. Phys. Chem.* **66** 283
- [3] Ando T, Fowler A B and Stern F 1982 *Rev. Mod. Phys.* **54** 437
- [4] Kim Y-H, Lee I-H, Nagaraja S, Leburton J-P, Hood R Q and Martin R M 2000 *Phys. Rev. B* **61** 5202
- [5] Chiodo L, Constantin L A, Fabiano E and Della Sala F 2012 *Phys. Rev. Lett.* **108** 126402
- [6] Pollack L and Perdew J P 1999 *J. Phys.: Condens. Matter* **12** 1239
- [7] Rajagopal A K, Kimball J C and Banerjee M 1978 *Phys. Rev. B* **18** 2339
- [8] Tanatar B and Ceperley D M 1989 *Phys. Rev. B* **39** 5005
- [9] Attaccalite C, Moroni S, Gori-Giorgi P and Bachelet G B 2002 *Phys. Rev. Lett.* **88** 256601
- [10] Pittalis S, Räsänen E, Vilhena J G and Marques M A L 2009 *Phys. Rev. A* **79** 012503
- [11] Vilhena J G, Räsänen E, Marques M A L and Pittalis S 2014 *J. Chem. Theory Comput.* **10** 1837
- [12] Jana S, Patra A and Samal P 2018 *Physica E* **97** 268
- [13] Jana S and Samal P 2017 *J. Phys. Chem. A* **121** 4804
- [14] Patra A, Jana S and Samal P 2018 *J. Chem. Phys.* **148** 134117
- [15] Patra A, Jana S and Samal P 2018 *J. Phys. Chem. A* **122** 3455
- [16] Hylleraas E A 1928 *Z. Phys.* **48** 469
- [17] Hylleraas E A 1929 *Z. Phys.* **54** 347
- [18] Hylleraas E A 1930 *Z. Phys.* **65** 209
- [19] Kinoshita T 1957 *Phys. Rev.* **105** 1490
- [20] Kinoshita T 1959 *Phys. Rev.* **115** 366
- [21] Koga T 1992 *J. Chem. Phys.* **96** 1276
- [22] Koga T, Kasai Y and Thakkar A J 1993 *Int. J. Quantum Chem.* **46** 689
- [23] Frankowski K and Pekeris C L 1966 *Phys. Rev.* **146** 46
- [24] Fruend D E, Huxtable B D and Morgan J D 1984 *Phys. Rev. A* **29** 980
- [25] Umrigar C J and Gonze X 1994 *Phys. Rev. A* **50** 3827

- [26] Drake G and Van Z-C 1994 *Chem. Phys. Lett.* **229** 486
- [27] Drake G W F, Cassar M M and Nistor R A 2002 *Phys. Rev. A* **65** 054501
- [28] Drake G W F 1999 *Phys. Scr.* **T83** 83
- [29] Chandrasekhar S 1944 *Astrophys. J.* **100** 176
- [30] Sech C L 1997 *J. Phys. B: At. Mol. Opt. Phys.* **30** L47
- [31] Tripathy D N, Padhy B and Kais D K 1995 *J. Phys. B: At. Mol. Opt. Phys.* **28** L41
- [32] Wu M-S 1982 *Phys. Rev. A* **26** 1762
- [33] Bhattacharyya S, Bhattacharyya A, Talukdar B and Deb N C 1996 *J. Phys. B: At. Mol. Opt. Phys.* **29** L147
- [34] Hehre W J, Stewart R F and Pople J A 1969 *J. Chem. Phys.* **51** 2657
- [35] Dunning T H 1989 *J. Chem. Phys.* **90** 1007
- [36] Jensen F 2001 *J. Chem. Phys.* **115** 9113
- [37] Giannozzi P *et al* 2009 *J. Phys.: Condens. Matter* **21** 395502
- [38] Chauhan R S and Harbola M K 2017 *Int. J. Quantum Chem.* **117** 25344
- [39] Singh R and Harbola M K 2017 *J. Chem. Phys.* **147** 144105
- [40] Chauhan R S and Harbola M K 2015 *Chem. Phys. Lett.* **639** 248
- [41] Taut M 1994 *J. Phys. A: Math. Theor.* **27** 1045
- [42] Taut M 1994 *J. Phys. A: Math. Theor.* **27** 4723
- [43] Taut M 1993 *Phys. Rev. A* **48** 3561
- [44] Taut M, Ernst A and Eschrig H 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** 2689
- [45] Patil S H 2008 *Eur. J. Phys.* **29** 517
- [46] Skobelev V V 2017 *J. Exp. Theor. Phys.* **125** 1058
- [47] Hirschfelder J O 1963 *J. Chem. Phys.* **39** 3145
- [48] Rontani M, Cavazzoni C, Bellucci D and Goldoni G 2006 *J. Chem. Phys.* **124** 124102
- [49] Makkonen I, Ervasti M M, Kauppila V J and Harju A 2012 *Phys. Rev. B* **85** 205140
- [50] Gylfadottir S S, Harju A, Jouttenus T and Webb C 2006 *New J. Phys.* **8** 211
- [51] Giannozzi P 2019 private communication
- [52] Čertík O, Pask J E and Vackář J 2013 *Comput. Phys. Commun.* **184** 1777
- [53] Kotochigova S, Levine Z H, Shirley E L, Stiles M D and Clark C W 1997 *Phys. Rev. A* **55** 191
- [54] Levy M, Perdew J P and Sahni V 1984 *Phys. Rev. A* **30** 2745
- [55] Pittalis S, Räsänen E and Marques M A L 2008 *Phys. Rev. B* **78** 195322
- [56] Ospadov E and Staroverov V N 2018 *J. Chem. Theory Comput.* **14** 4246
- [57] Lehtola S, Steigemann C, Oliveira M J and Marques M A 2018 *SoftwareX* **7** 1
- [58] Perdew J P, Parr M L R G and Balduz J J L 1982 *Phys. Rev. Lett.* **49** 1691