

# A compact boundary-condition-determined wavefunction for two-electron atomic systems

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## Abstract

Highly compact wavefunctions with a clear physical meaning for the He atom and He-like isoelectronic ions for  $Z = 1-10$  are written as a symmetrized product of  $\exp[(ar + br^2)/(1 + r)]$  electron–nucleus terms and an electron–electron Jastrow factor to satisfy the correct asymptotic behaviour both at short and long interparticle distances. Some parameters are chosen to satisfy exactly the cusp conditions, while the others are optimized by variational Monte Carlo calculations. The wavefunction energy is within 2 millihartrees from the non-relativistic limit in the entire  $Z$ -range, improving previously published work on similar compact wavefunctions. We tested the validity of the ‘coalescence wavefunction’ approximation. The  $Z$ -dependence of the optimized parameters allows us to write a general form of the wavefunction, using  $Z$  as an explicit parameter and four parameters independent of  $Z$ . We checked the validity of this wavefunction on the case  $Z = 30$ .

## 1. Introduction

Despite the fact that almost 80 years have passed since the first pioneering calculations by Hylleraas [1] on the helium atom, the search for accurate, but nevertheless compact, wavefunctions with a clear physical meaning has not ended. Surely there is no shortage of extremely accurate wavefunctions for the helium atom and some two-electron atomic ions [2–4]. The most recent record is an impressive 40 digit accuracy by Nakashima and Nakatsuji [4]. However, as noted long time ago by Mulliken [5] just at the dawn of the massive use of computers in chemistry for electronic structure calculations, ‘... the more accurate the calculations became, the more the concepts tended to vanish into thin air’. Furthermore, processes such as for example double ionization or  $(e, 2e)$  are strongly influenced by the electron correlation, but the evaluation of cross sections requires numerical integration and this task cannot be realized using two-electron wavefunctions with thousands of terms. For these reasons the search for compact and accurate explicitly correlated functions for two and more electron systems is still an active area of research [6–11].

In the past, the importance of the Kato cusp conditions in the construction of an accurate wavefunction has been stressed several times [12, 13]. However, only recently the importance of other boundary conditions that the exact wavefunction must satisfy has been pointed out [14–18].

Kleinekathöfer and co-workers [6] were the first, to our knowledge, to systematically study the inclusion of both cusp conditions and large  $r$  asymptotic conditions for the wavefunctions of two-electron atoms and ions for  $Z = 1-10$ . Using a kind of exponentially correlated wavefunction, with one variational parameter, they computed energies within 2.1–6.8 millihartrees from the exact values.

Explicitly correlated wavefunctions for small systems using an exponential or Jastrow correlated form have been used for quite some time, especially in the field of variational and diffusion Monte Carlo calculations [19–21]. These correlation factors have been recently rediscovered [22] in the field of explicitly correlated methods denoted by F12 methods and shown to greatly improve the convergence over the previously R12 methods that employed a linear function. The ultimate reason for the very fast convergence of these kinds of functions to the exact ground state seems to be the fact that these forms

give a convergent perturbation theory [23, 24] as opposed to other functional forms.

## 2. The construction of the wavefunction

Within the Born–Oppenheimer approximation, the non-relativistic Hamiltonian operator for two-electron systems is

$$H = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \quad (1)$$

where  $Z$  is the nuclear charge.

At particles' coalescence [25] the exact ground state wavefunction behaves as

$$\frac{1}{\Psi} \frac{\partial \Psi}{\partial r_{ij}} \Big|_{r_{ij}=0} = c \quad (2)$$

where  $c$  is a constant, depending on the type of the colliding particles. In our case,  $c = 1/2$  for electron–electron, while  $c = -Z$  for electron–nucleus.

The local solution of equation (2) suggests that a good trial wavefunction should have the following asymptotic behaviour, when one electron is close to the nucleus,

$$\begin{aligned} \Psi(r_1, r_2, r_{12}) &\xrightarrow{r_1 \rightarrow 0} \exp(-Zr_1)G(r_2) \\ \Psi(r_1, r_2, r_{12}) &\xrightarrow{r_2 \rightarrow 0} \exp(-Zr_2)G(r_1), \end{aligned} \quad (3)$$

and the following behaviour when two electrons are close to each other,

$$\Psi(r_1, r_2, r_{12}) \xrightarrow{r_{12} \rightarrow 0} \exp(r_{12}/2)F(r_1), \quad (4)$$

where  $G$  and  $F$  are unknown functions. Note that since some interparticle distances are zero, it is possible to rewrite the argument of the unknown functions using different variables.

The second property that we wish to incorporate into the trial wavefunction is the correct asymptotic behaviour when one of the particles goes to infinity.

If the second electron is very far from the nucleus, we can write the wavefunction as  $\Psi = \exp(f_1(r_1) + f_2(r_2))$ . The local energy  $E_L(\mathbf{R}) = H\Psi(\mathbf{R})/\Psi(\mathbf{R})$  is

$$\begin{aligned} -\frac{1}{2}f_1''(r_1) - \frac{1}{2}f_1'(r_1)^2 - \frac{f_1'(r_1)}{r_1} - \frac{1}{2}f_2''(r_2) \\ - \frac{1}{2}f_2'(r_2)^2 - \frac{f_2'(r_2)}{r_2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}. \end{aligned} \quad (5)$$

As before, the electron–nucleus cusp must be imposed on  $f_1(r_1)$ .

For  $r_2 \rightarrow \infty$ ,  $r_{12} \rightarrow r_2$ , we have  $E_L(r_1) + E_L(r_2) = E_0$ . In order for this equation to be fulfilled, since the two local energies depend on different variables, we must equate them to different constants. So we can write

$$E_L(r_1) = E_1 \quad E_L(r_2) = E_2 \quad E_1 + E_2 = E_0. \quad (6)$$

Now consider the asymptotic behaviour of  $f_2(r_2)$

$$f_2(r_2) \rightarrow -\alpha r_2 - \beta \log(r_2). \quad (7)$$

Substituting we get

$$-\frac{\alpha^2}{2} + \frac{\beta(1-\beta)}{2r_2^2} + \frac{1+\alpha-\alpha\beta-Z}{r_2} = E_2. \quad (8)$$

To recover the asymptotic solution we discard the  $r_2^{-2}$  term, impose the  $r_2^{-1}$  term to vanish and solve for  $\alpha$ . We obtain

$$\alpha = \sqrt{-2E_2}, \quad \beta = 1 + \frac{Z-1}{\alpha}. \quad (9)$$

The second electron sees an effective charge of  $(Z-1)$ , while the first one belongs to a hydrogenoid atom with energy  $E_1 = -Z^2/2$ , so  $E_2 = E_0 + Z^2/2$ .

A function  $\exp(f_2(r_2)) = r_2^{-\beta} \exp(-\alpha r_2)$  is correct for  $r_2 \rightarrow \infty$ , but the  $r_2^{-\beta}$  term is troublesome at short distances and does not allow satisfying the electron–nucleus cusp condition. As increasing  $Z$  the value of  $\beta$  increases only slightly staying less than 2, while  $\alpha$  goes up quickly, we can approximate

$$\exp(f_2(r_2)) \approx \exp(-\alpha r_2). \quad (10)$$

Based on the above conditions, a single-particle function describing the motion of the electron in the field of the Hydrogen-like system should behave as  $\exp(-Zr)$  when  $r \rightarrow 0$  (equation (3)) and as  $\exp(-\alpha r)$  when  $r \rightarrow \infty$  (equation (10)).

What is new in this work is the functional form  $f(r) = \exp\left(\frac{ar+br^2}{1+r}\right)$  we adopt, which enables us to satisfy both the asymptotic conditions exactly by a particular choice of parameters. A function with slightly more variational freedom is  $f(r) = \exp\left(\frac{ar+br^2}{1+cr}\right)$ , in this case the asymptotic condition for  $r \rightarrow \infty$  only defines the ratio  $b/c$ . We did not employ this functional form in the present work.

As to the pair functions describing the electron–electron part, in order to satisfy the cusp conditions in equation (4), they should behave, for  $r_{12} \rightarrow 0$ , like an exponential with an appropriate parameter, while for  $r_{12} \rightarrow \infty$  it is a common choice, although not mathematically required, to direct the function to a constant value. A Jastrow factor  $g(r) = \exp\left(\frac{dr}{1+er}\right)$  can satisfy these conditions.

These functional forms have already been used in the field of variational and diffusion Monte Carlo calculations, as basis set more flexible than standard atomic orbitals and as electron–electron correlation factor to reduce the variance. Here we explore their performance when most parameters are fixed to satisfy the asymptotic conditions.

Having defined the single-particle functions and the correlation factor we are going to use, we must decide the overall structure of the many-body wavefunction. The common choice of doubly-occupied single particle orbitals times a correlation factor

$$\Psi(1, 2) = \varphi(r_1)\varphi(r_2)g(r_{12}) \quad (11)$$

is not able to satisfy both asymptotic conditions for  $r \rightarrow \infty$  and  $r \rightarrow 0$ , as noted by Patil [26].

Eckart [27] was the first to use the form

$$\Psi(1, 2) = (1 + P_{12})\varphi_1(r_1)\varphi_2(r_2) \quad (12)$$

where  $\hat{P}_{12}$  is the operator that permutes the two electrons. This wavefunction is able, for appropriate choices of the single-particle functions, to satisfy the asymptotic conditions.

However, Eckart used the form

$$\Psi(1, 2) = \exp(-ar_1 - br_2) + \exp(-br_1 - ar_2) \quad (13)$$

and with this choice of the single-particle functions it is not possible to satisfy the asymptotic conditions (it is easy to see, for example, that the electron–nucleus cusp conditions can be satisfied only if both  $a$  and  $b$  are set equal to  $-Z$ ). Eckart optimized both coefficients variationally. Of course, nothing changes if we add a correlation factor.

Here, we use a simple wavefunction that includes all two-particle correlations

$$\Psi(r_1, r_2, r_{12}) = (1 + \hat{P}_{12})f_1(r_1)f_2(r_2)g(r_{12}). \quad (14)$$

This functional form has been used with success in the past to study some few-body systems [28, 29].

In explicit form, the wavefunction reads

$$\begin{aligned} \Psi(r_1, r_2, r_{12}) = & (1 + \hat{P}_{12}) \exp\left(\frac{a_1 r_1 + b_1 r_1^2}{1 + r_1}\right) \\ & \times \exp\left(\frac{a_2 r_2 + b_2 r_2^2}{1 + r_2}\right) \exp\left(\frac{dr_{12}}{1 + er_{12}}\right). \end{aligned} \quad (15)$$

Let us now examine how this wavefunction can be simplified constraining it to satisfy the correct asymptotic behaviour and the various cusp conditions.

In order to satisfy all the cusp conditions, we must fix the parameters  $a_1$ ,  $a_2$  and  $d$ :

$$\begin{aligned} \Psi(1, 2) = & (1 + \hat{P}_{12}) \exp\left(\frac{-Zr_1 + b_1 r_1^2}{1 + r_1}\right) \\ & \times \exp\left(\frac{-Zr_2 + b_2 r_2^2}{1 + r_2}\right) \exp\left(\frac{r_{12}/2}{1 + er_{12}}\right). \end{aligned} \quad (16)$$

Let us consider the asymptotic form of our trial function for  $r_2 \rightarrow \infty$  (or  $r_1 \rightarrow \infty$ ). Since  $r_{12} \approx r_2 \rightarrow \infty$ , the correlation factor becomes constant

$$\begin{aligned} \Psi(1, 2) \xrightarrow{r_2 \rightarrow \infty} & \exp\left(\frac{-Zr_1 + b_1 r_1^2}{1 + r_1}\right) \exp(b_2 r_2) \\ & + \exp\left(\frac{-Zr_1 + b_2 r_1^2}{1 + r_1}\right) \exp(b_1 r_2). \end{aligned} \quad (17)$$

Assuming, to fix the ideas, that  $|b_2| < |b_1|$ , we obtain

$$\Psi(1, 2) \xrightarrow{r_2 \rightarrow \infty} \exp\left(\frac{-Zr_1 + b_1 r_1^2}{1 + r_1}\right) \exp(b_2 r_2). \quad (18)$$

As required, there is a correct exponential decay of the wavefunction for large values of the distance of one of the electrons. The exponent  $b_2$  in the exact wavefunction is related to the ionization potential. However, our wavefunction being an approximated one, we do not expect this relation to hold exactly and prefer to treat it as a variational parameter and optimize it.

The factor that depends on electron 1 should describe the remaining one-electron system. We have the choice of imposing exactly this asymptotic condition, setting  $b_1 = -Z$  in equation (16) we get correctly a hydrogenoid function for electron 1:

$$\begin{aligned} \Psi_2(1, 2) = & (1 + \hat{P}_{12}) \exp(-Zr_1) \\ & \times \exp\left(\frac{-Zr_2 + b_2 r_2^2}{1 + r_2}\right) \exp\left(\frac{r_{12}/2}{1 + er_{12}}\right). \end{aligned} \quad (19)$$

$\Psi_2$  has only two variational parameters,  $b_2$  and  $e$ : we have gained physical insight into the wavefunction, but lost

variational freedom. The second choice is to optimize variationally the parameter  $b_1$ , since this factor must describe the behaviour of the first electron not only when the second is far away.

$$\begin{aligned} \Psi_3(1, 2) = & (1 + \hat{P}_{12}) \exp\left(\frac{-Zr_1 + b_1 r_1^2}{1 + r_1}\right) \\ & \times \exp\left(\frac{-Zr_2 + b_2 r_2^2}{1 + r_2}\right) \exp\left(\frac{r_{12}/2}{1 + er_{12}}\right), \end{aligned} \quad (20)$$

with three variational parameters,  $b_1$ ,  $b_2$  and  $e$ .

The general form

$$\Psi(1, 2) = (1 + \hat{P}_{12})\phi_0(r_1)f(r_2)g(r_{12}) \quad (21)$$

where  $\phi_0(r) = \exp(-Zr)$  is the ground-state wavefunction for the remaining hydrogenoid system when one electron is stripped away, has been used in the past, but not very often. It has the advantage of having a clear physical insight into the structure of the system. For this reason this form has been given the name ‘coalescence wavefunction’ by Chen *et al* [30]. For more complex systems the wavefunction can be assembled recursively [8].

### 3. Results and discussion

Since the form chosen for the wavefunction makes it impossible to analytically compute the overlap and Hamiltonian integrals, we used the well-known variational Monte Carlo (VMC) technique [31, 32] to estimate the value of the variational energy.

The parameters of both types of wavefunction were first roughly optimized by minimizing the mean absolute deviation of the local energy [33], a robust variant of the more common variance optimization, and then fine tuned with an energy optimization. The parameters show a marked linear dependence on the atomic charge. The  $e$  parameters of the Jastrow factor, for both types of wavefunctions, when plotted as a function of  $Z$  and fitted by a linear function, give an intercept very close to zero. We decided to constrain the curve to pass through zero:  $e = k_1 Z$ . In this way the function  $\exp\left(\frac{1}{2} \frac{r_{12}}{1+k_1 Z r_{12}}\right)$  for  $Z \rightarrow 0$  converges to  $\exp\left(\frac{1}{2} r_{12}\right)$  which is, formally, the exact solution for the problem of two interacting electrons as  $Z \rightarrow 0$ . The parameter  $b_1$ , in  $\Psi_3$ , also gives a negligible intercept and we forced it to be zero, the rationale being that for  $Z \rightarrow 0$  the function  $f(r_1)$  should attain a constant value, and this is achieved by writing  $f(r_1) = \exp\left(\frac{-Zr_1 + Zk_2 r_1^2}{1+r_1}\right)$ . The  $b_2$  parameters, for both  $\Psi_2$  and  $\Psi_3$ , fit well with a linear function that intersects the  $y$ -axis closely, but statistically different from zero. The  $b_2$  parameter, as we saw earlier, is directly related to the decay of the wavefunction for large  $r$ . If we had the exact wavefunction this would imply  $b_2 = -\sqrt{-2E_0 - Z^2}$ . Since the ground-state energy depends quadratically on the nuclear charge, we should expect an almost linear behaviour, as  $Z$  increases. Our functional form of course does not comprise the exact one, but nevertheless we observe a linear behaviour, not only for large  $Z$ , but in the entire range.

**Table 1.** Energies (hartree) of two-electron atomic systems.

$Z$	$E^a$	$E^b$	$E^c$	$E^d$	$E^e$
1	-0.527751		-0.5265	-0.52582(1)	-0.52671(1)
2	-2.903724	-2.9017(4)	-2.9000	-2.90057(1)	-2.90266(1)
3	-7.279913	-7.271(1)	-7.2749	-7.27685(2)	-7.27865(1)
4	-13.655566	-13.642(1)	-13.6499	-13.65259(2)	-13.65412(2)
5	-22.030972	-22.014(2)	-22.0249	-22.02809(2)	-22.02934(2)
6	-32.406247	-32.386(3)	-32.4000	-32.40343(3)	-32.40449(2)
7	-44.781445	-44.755(3)	-44.7750	-44.77866(3)	-44.77957(2)
8	-59.156595	-59.129(4)	-59.1500	-59.15384(4)	-59.15461(3)
9	-75.531712	-75.502(4)	-75.5250	-75.52897(4)	-75.52968(3)
10	-93.906807	-93.875(5)	-93.9000	-93.90408(8)	-93.90469(5)

<sup>a</sup> Non-relativistic limit from [4].

<sup>b</sup> Best results in table 3 from [30].

<sup>c</sup> From [6].

<sup>d</sup> Present work: two optimized parameters.

<sup>e</sup> Present work: three optimized parameters.

For the two-parameter wavefunction  $\Psi_2$  we have  $b_2 = 0.4193 - 0.8841Z$  and  $e = 0.2600Z$ , while for the three-parameter wavefunction  $\Psi_3$ ,  $b_1 = -1.0778Z$ ,  $b_2 = 0.4142 - 0.8287Z$  and  $e = 0.2247Z$ . All linear fits have a coefficient of determination  $r^2$  greater than 0.999.

The coefficient in  $b_1$  evidences that  $\Psi_3$  is only slightly different from  $\Psi_2$ , that is the coalescence wavefunction is only perturbed by the introduction of extra flexibility in the wavefunction. The linear dependence of  $b$  and  $e$  on  $Z$  allows us to derive a general expression for two-electron atomic wavefunctions where  $Z$  is a parameter and the constants are independent of  $Z$ :

$$\Psi(1, 2|Z) = (1 + \hat{P}_{12}) \exp\left(\frac{-Zr_1 + Zk_2r_1^2}{1 + r_1}\right) \times \exp\left(\frac{-Zr_2 + (k_3 + Zk_4)r_2^2}{1 + r_2}\right) \exp\left(\frac{r_{12}/2}{1 + Zk_1r_{12}}\right) \quad (22)$$

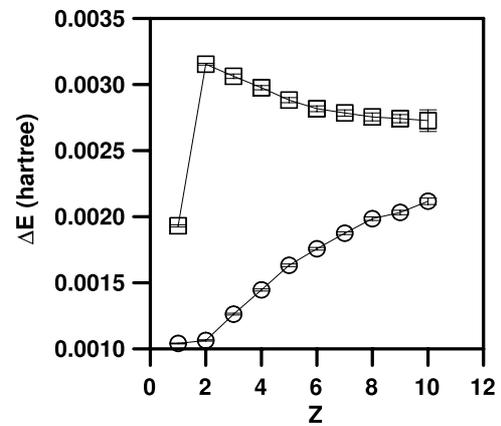
where  $k_1 = 0.2247$ ,  $k_2 = -1.0778$ ,  $k_3 = 0.4142$  and  $k_4 = -0.8287$ .

This functional form has the correct asymptotic form when  $Z \rightarrow \infty$ , that is  $\exp(-Zr_1 - Zr_2)$ .

The values of  $b_2$  for  $\Psi_2$  are always smaller than the theoretical value  $\sqrt{-2E_i}$ , indicating a smoother asymptotic decay of the wavefunction. The differences between their values and the theoretical ones increase with  $Z$  up to a maximum of 10%.

Our results are compared in table 1 with the non-relativistic limits computed by Nakashima and Nakatsuji [4], the results of Chen *et al* [30] and those of Kleinekathofer *et al* [6]. These values were selected among all the results on two-electron systems as obtained by very compact wavefunctions, in the spirit of this work.

The two-parameter coalescence wavefunction  $\Psi_2$  gives good energies in the whole range  $Z = 1-10$ : it substantially improves all energy values, except for He, of the coalescence wavefunction used by Chen *et al* [30], and those, except for  $H^-$ , computed by Kleinekathofer *et al* [6]. A graphical representation of the quality of the wavefunction can be seen in figure 1 (squares), where the difference between the recovered energy and the non-relativistic limit is plotted against the nuclear charge.



**Figure 1.** Difference between the calculated energy and the non-relativistic limit; two (squares) and three (circles) variational parameters.

From the picture it is immediately clear that a coalescence wavefunction type has an overall good quality (about 3 millihartrees from the exact energy), but behaves much better for the negative ion  $H^-$  than for the neutral He atom or the positively charged ions. The reason [8] is that the hydrogen negative ion can be very well described by a pure hydrogen atom and a second electron orbiting around, while increasing the nuclear charge the two electrons are more attracted towards the nucleus and must necessarily be at a closer distance.

By allowing the tail of the inner electron orbital to be optimized, having three variational parameters, the quality of the wavefunction is further improved, with energies better than those computed by Chen *et al* [30] and by Kleinekathofer *et al* [6] in their investigations of accurate, but compact wavefunctions for two-electron systems. As before, a graphical representation (see figure 1) is more revealing. The deviation from the exact energy, as a function of  $Z$ , is between 1 and 2 millihartrees.

Upon increasing  $Z$  the difference between the energies computed by  $\Psi_2$  and  $\Psi_3$  decreases: the larger the  $Z$ , the more compact is the wavefunction, and for small values of  $r$  the effect of the  $r^2$  term is negligible. The quality of the wavefunction by Chen *et al* [30] decreases as  $Z$  increases, while

ours remains approximately constant. For this reason it is likely that we have reached, or are very close, to the theoretical limit of the variational energy that can be recovered by the functional form  $\Psi(r_1, r_2, r_{12}) = (1 + \hat{P}_{12})f_1(r_1)f_2(r_2)g(r_{12})$ . Further improvement should explicitly incorporate three-body terms.

As to the linear dependence of  $b$  and  $e$  parameters on  $Z$ , a further check of its validity was realized extrapolating to  $Z=30$  and computing the energies without further optimization. The non-relativistic limit was estimated to be  $-881.4062(1)$  hartree by a diffusion Monte Carlo simulation. The variational energy for  $\Psi_2$  is  $-881.4043(1)$  hartree, while for  $\Psi_3$  is  $-881.4045(1)$  hartree. These values are as expected near to the exact limit and their difference is less than those computed for smaller  $Z$ , as anticipated from the trends in figure 1.

#### 4. Conclusions

We have proposed two kinds of accurate, but compact, wavefunctions for two-electron systems, having a clear physical interpretation and with all the boundary conditions satisfied. The energy of the three-parameter wavefunction is within 2 millihartrees from the non-relativistic limit and is better than previously published work. As the parameters of our wavefunctions, plotted as a function of the nuclear charge  $Z$ , show a linear trend, the wavefunction for two-electron atoms can be written in a very general form that does not need to be optimized each time for a given  $Z$  value.

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