Accurate *S*-state helium wave functions in momentum space

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High-accuracy helium wave functions based on exponentials with random coefficients are transformed into momentum space. The utility of the wave functions is demonstrated through calculation of the expectation value of various operators needed to evaluate relativistic and QED corrections.

I. INTRODUCTION

In recent years a basis set consisting of random exponentials has been used with increasing frequency to carry out calculations in helium [1–3]. For singlet and triplet *S* states it can be written as

$$\phi(\vec{r}_1, \vec{r}_2) = \sum_i C_i [e^{-\alpha_i r_1 - \beta_i r_2 - \gamma_i r_{12}} \pm e^{-\alpha_i r_2 - \beta_i r_1 - \gamma_i r_{12}}], \quad (1)$$

where α_i, β_i, and γ_i are parameters that are chosen randomly in certain ranges, and the spin wave functions are understood. Through careful choice of those ranges Korobov [1] has been able to obtain a ground state energy of

$$E = -2.903\ 724\ 377\ 034\ 119\ 598\ 311\ 159 \text{ a.u.} \quad (2)$$

While even higher accuracies are possible with basis sets that incorporate known nonanalytic behaviors of the wave function [4], the simple form of the above wave function makes the evaluation of higher-order corrections coming from relativistic and QED corrections relatively straightforward. In this note we will present calculations based on the momentum space form of Eq. (1), where the wave function is defined through

$$\phi(\vec{p}_1, \vec{p}_2) = \int \frac{d^3 r_1 d^3 r_2}{(2\pi)^3} e^{-i\vec{p}_1 \cdot \vec{r}_1} e^{-i\vec{p}_2 \cdot \vec{r}_2} \phi(\vec{r}_1, \vec{r}_2). \quad (3)$$

The Fourier transform is evaluated by first noting that

$$e^{-\alpha r_1 - \beta r_2 - \gamma r_{12}} = -\frac{\partial^3}{\partial \alpha \partial \beta \partial \gamma} \frac{e^{-\alpha r_1 - \beta r_2 - \gamma r_{12}}}{r_1 r_2 r_{12}}$$
$$= -\frac{\partial^3}{\partial \alpha \partial \beta \partial \gamma} \int \frac{d^3 q_1}{2\pi^2} \frac{e^{i\vec{q}_1 \cdot \vec{r}_1}}{\vec{q}_1^2 + \alpha^2} \int \frac{d^3 q}{2\pi^2} \frac{e^{i\vec{q} \cdot \vec{r}_{12}}}{\vec{q}^2 + \gamma^2}$$
$$\times \int \frac{d^3 q_2}{2\pi^2} \frac{e^{i\vec{q}_2 \cdot \vec{r}_2}}{\vec{q}_2^2 + \beta^2}. \quad (4)$$

To simplify the following discussion, we Fourier transform only the above expression, and define it as $\phi_i(\vec{p}_1, \vec{p}_2)$, with the generalization to Eq. (1) being clear. We see that

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$$\phi_i(\vec{p}_1, \vec{p}_2) = -\frac{1}{\pi^3} \frac{\partial^3}{\partial \alpha \partial \beta \partial \gamma} \int d^3 q \frac{1}{(\vec{p}_1 - \vec{q})^2 + \alpha^2}$$
$$\times \frac{1}{\vec{q}^2 + \gamma^2} \frac{1}{(\vec{p}_2 + \vec{q})^2 + \beta^2}. \quad (5)$$

The integral over $d^3 q$ has been carried out analytically in Ref. [5] and leads to

$$\phi_i(\vec{p}_1, \vec{p}_2) = -\frac{2}{\pi} \frac{\partial^3}{\partial \alpha \partial \beta \partial \gamma} \frac{\theta}{\sqrt{x}}, \quad (6)$$

where

$$y = \gamma [|\vec{p}_2 + \vec{p}_1|^2 + (\alpha + \beta)^2] + \beta(\gamma^2 + \alpha^2 + \vec{p}_1^2)$$
$$+ \alpha(\gamma^2 + \beta^2 + \vec{p}_2^2),$$
$$x = [|\vec{p}_2 + \vec{p}_1|^2 + (\alpha + \beta)^2][\vec{p}_1^2 + (\alpha + \gamma)^2]$$
$$\times [\vec{p}_2^2 + (\beta + \gamma)^2] - y^2,$$

$$\theta = \arctan\left(\frac{\sqrt{x}}{y}\right). \quad (7)$$

While this equation for $\phi_i(\vec{p}_1, \vec{p}_2)$ seems quite compact, the action of the three derivatives leads to a considerably more complicated expression. It simplifies if we introduce the auxiliary parameters

$$X_1 = \frac{dx}{d\alpha}, \quad X_2 = \frac{dx}{d\beta}, \quad X_3 = \frac{dx}{d\gamma};$$

$$Y_1 = \frac{dy}{d\alpha}, \quad Y_2 = \frac{dy}{d\beta}, \quad Y_3 = \frac{dy}{d\gamma};$$

$$X_{23} = \frac{d^2 x}{d\beta d\gamma}, \quad X_{12} = \frac{d^2 x}{d\alpha d\beta}, \quad X_{13} = \frac{d^2 x}{d\alpha d\gamma};$$

$$T_1 = X_1 X_{23} + X_2 X_{13} + X_3 X_{12}, T_2 = X_1 + X_2 + X_3,$$

$$T_3 = Y_1 X_{23} + Y_2 X_{13} + Y_3 X_{12}, \quad T_4 = Y_1 + Y_2 + Y_3,$$

$$T_5 = X_1 Y_2 Y_3 + X_2 Y_1 Y_3 + X_3 Y_1 Y_2,$$

$$T_6 = Y_1 X_2 X_3 + Y_2 X_1 X_3 + Y_3 X_1 X_2. \quad (8)$$

In terms of these we find

$$\phi_i(\vec{p}_1,\vec{p}_2) = -\frac{2}{\pi}\left[\frac{3\theta}{8x^{7/2}}[2xT_1 - 5X_1X_2X_3] + \frac{y''(T_2 + 2yT_4)}{D^2}\right.$$

$$+\frac{T_3}{D^2} - \frac{4yT_5}{D^3} + \frac{2(x-3y^2)Y_1Y_2Y_3}{D^3}$$

$$+\frac{(40xy^3 + 33x^2y + 15y^5)X_1X_2X_3}{8x^3D^3}$$

$$\left.-\frac{yT_1(3y^2+5x)}{4x^2D^2} - \frac{2T_1}{D^3} - \frac{2}{D}\right], \tag{9}$$

where $D = x + y^2$ and $y'' = 2(\alpha + \beta + \gamma)$. We note the following symmetry properties of the momentum space wave function. Because the basic functions that form the wave function, x and y, are invariant under the simultaneous replacement $\vec{p}_1 \leftrightarrow \vec{p}_2$ and $\alpha \leftrightarrow \beta$, for singlet states $\phi(\vec{p}_1,\vec{p}_2) = \phi(\vec{p}_2,\vec{p}_1)$ and for triplet states $\phi(\vec{p}_1,\vec{p}_2) = -\phi(\vec{p}_2,\vec{p}_1)$. Both symmetries also hold when the magnitudes of $\vec{p}_1$ and $\vec{p}_2$ are switched.

There are various uses for the wave function of helium in momentum space, notably application to scattering calculations. While most work has been carried out with Fourier transforms of Hartree-Fock wave functions, an approach that includes correlation more completely is given in Ref. [6]. In that work, a Hylleraas basis set was Fourier transformed and applied to the calculation of a number of helium properties, notably the Compton profile. While the wave function used here gives a more accurate energy (odd powers of r_{12} were not included in the basis set of Ref. [6]), we do not find appreciably different answers for any of the quantities calculated there. In particular, we find the same small difference between using fully correlated wave functions and Hartree-Fock wave functions for the Compton profile. Rather than pursuing this line of research we instead now discuss applications of the momentum space wave function to the calculation of higher-order relativistic and QED corrections to the energies of the 1 ${}^1S_0$, 2 ${}^1S_0$, and 2 ${}^3S_1$ states of neutral helium.

These corrections are obtained from a set of operators O_i, with associated energy shifts $E_i = \langle \phi | O_i | \phi \rangle$. The first set of operators was derived by Breit [7], and describe corrections of order α^2 a.u. The equation he used in the derivation has certain difficulties connected with negative energy states [8], but later treatments using the Bethe-Salpeter equation [9–11] treat negative energy states consistently and allow the systematic treatment of higher-order corrections.

Most recent calculations, however, use the technique of effective field theory [12] to derive the operators. We note in particular the compact rederivation of the Douglas-Kroll [11] results for contributions to the fine structure of helium in order α^4 a.u. of Ref. [13], and the derivation of contributions to the energy of the ground state to the same order in Ref. [14]. The idea of effective-field theory is to compare free-particle scattering amplitudes in QED to an effective nonrelativistic theory, with operators added to the Schrödinger Hamiltonian that account perturbatively for the difference of the amplitudes. Once the operators have been determined from considering free-particle scattering, they are used as perturbations in standard bound-state Rayleigh-Schrödinger

perturbation theory to calculate energy shifts. In this approach it is natural to work in momentum space, and the operators are then Fourier transformed to coordinate space for numerical evaluation. Here, however, because we have formed wave functions in momentum space, we avoid this step, and work exclusively in momentum space. This has the advantage of simplicity, but the disadvantage of being less accurate than coordinate space. We now give a brief rederivation of the Breit operators using effective-field theory, and illustrate their numerical evaluation in momentum space.

The connection of the scattering amplitude of two electrons with momenta p_1 and p_2 to scatter into states with momenta p_3 and p_4 to an energy shift is

$$E_i = \frac{1}{(2\pi)^6}\int d^3p_1 d^3p_2 d^3p_3 d^3p_4 \phi^*(\vec{p}_3,\vec{p}_4)$$

$$\times O_i(\vec{p}_3,\vec{p}_4;\vec{p}_1,\vec{p}_2)\phi(\vec{p}_1,\vec{p}_2). \tag{10}$$

We work in the center-of-mass frame, with initial nuclear momentum $-\vec{p}_1 - \vec{p}_2$ and final nuclear momentum $-\vec{p}_3 - \vec{p}_4$. If only electron-electron interactions (e-e) are considered, momentum conservation allows us to write

$$O_i^{e\text{-}e}(\vec{p}_3,\vec{p}_4;\vec{p}_1,\vec{p}_2)$$

$$= (2\pi)^3\delta^3(\vec{p}_3 + \vec{p}_4 - \vec{p}_1 - \vec{p}_2)M_i^{e\text{-}e}(\vec{p}_3;\vec{p}_1,\vec{p}_2) \tag{11}$$

with the associated energy shift

$$E_i^{e\text{-}e} = \frac{1}{(2\pi)^3}\int d^3p_1 d^3p_2 d^3p_3 \phi^*(\vec{p}_3,\vec{p}_1 + \vec{p}_2 - \vec{p}_3)$$

$$\times M_i^{e\text{-}e}(\vec{p}_3;\vec{p}_1,\vec{p}_2)\phi(\vec{p}_1,\vec{p}_2). \tag{12}$$

If instead we consider diagrams in which one of the electrons, taken to be electron 1, interacts with the nucleus (e-N), and electron 2 does not participate, we can write

$$O_i^{e\text{-}N}(\vec{p}_3,\vec{p}_4;\vec{p}_1,\vec{p}_2) = (2\pi)^3\delta^3(\vec{p}_4 - \vec{p}_2)M_i^{e\text{-}N}(\vec{p}_3,\vec{p}_1) \tag{13}$$

with the energy shift

$$E_i^{e\text{-}N} = \frac{1}{(2\pi)^3}\int d^3p_1 d^3p_2 d^3p_3 \phi^*(\vec{p}_3,\vec{p}_2)$$

$$\times M_i^{e\text{-}N}(\vec{p}_3,\vec{p}_1)\phi(\vec{p}_1,\vec{p}_2). \tag{14}$$

Diagrams with all three particles interacting have no δ functions, and have to be evaluated with the 12-dimensional integral of Eq. (10). In all cases we note that three of the integration variables can be carried out trivially, and that the adaptive Monte Carlo program VEGAS [15] can be used to numerically evaluate the integrals, though with far less accuracy than available from coordinate-space techniques. This loss of accuracy is due entirely to the fact that the multidimensional integrals have to be carried out numerically: the wave functions themselves are quite accurate. In the calculations presented here we use 600 basis functions, and the energy eigenvalues are accurate to more than 14 digits for the ground state and 11 for the excited S states.

TABLE I. Expectation of operators for $n=1$ and 2 S states of helium in units of α^2 a.u. The notation H_2 in $E_{DT}{}^{e\text{-}e}$ indicates the δ function is not included in the result.

Operator	$1\,{}^1S_0$	$2\,{}^1S_0$	$2\,{}^3S_1$
$E_{RMI}{}^{e\text{-}e}$	$-13.5212(3)$	$-10.27959(5)$	$-10.45887(4)$
$E_{DC}{}^{e\text{-}e}$	$0.3346(3)$	$0.02718(8)$	0.0
$E_{DC}{}^{e\text{-}N}$	$5.6879(2)$	$4.1139(2)$	$4.1479(2)$
$E_{DT}{}^{e\text{-}e}(H_2)$	$-0.1393(2)$	$-0.00922(1)$	$-0.00157(7)$

We begin by evaluating the relativistic mass increase (RMI) operator, which we treat as an e-e diagram. The contribution to the scattering amplitude of this operator is

$$M_{RMI}{}^{e\text{-}e}(\vec{p}_3;\vec{p}_1,\vec{p}_2) = -(2\pi)^3\frac{p_1^4+p_2^4}{8m^3}\delta(\vec{p}_3-\vec{p}_1), \quad (15)$$

which gives the energy shift

$$E_{RMI}{}^{e\text{-}e} = -\frac{1}{8m^3}\int d^3p_1 d^3p_2 \phi^*(\vec{p}_1,\vec{p}_2)(p_1^4+p_2^4)\phi(\vec{p}_1,\vec{p}_2). \quad (16)$$

The result is tabulated in the first row of Table I.

We next turn to corrections to Coulomb scattering between the electrons. In this case the nonrelativistic scattering operator is

$$M_C{}^{e\text{-}e}(\vec{p}_3;\vec{p}_1,\vec{p}_2) = \frac{4\pi\alpha}{|\vec{p}_3-\vec{p}_1|^2}. \quad (17)$$

This corresponds to the coordinate space potential $\alpha/|\vec{r}_1-\vec{r}_2|$. To calculate relativistic corrections, we use Dirac spinors to describe scattering and work in Coulomb gauge. We introduce the notation DC to refer to the scattering amplitude with exchange of a Coulomb photon, and DT for the scattering amplitude with exchange of a transverse photon. The DC scattering amplitude can then be Taylor expanded in powers of p/m, with the leading corrections given by

$$M_{DC}{}^{e\text{-}e}(\vec{p}_3;\vec{p}_1,\vec{p}_2) = M_C{}^{e\text{-}e}(\vec{p}_3;\vec{p}_1,\vec{p}_2)\left[1-\frac{|\vec{p}_3-\vec{p}_1|^2}{8m^2}\right.$$
$$-\frac{|\vec{p}_4-\vec{p}_2|^2}{8m^2}+\frac{i\vec{\sigma}_1\cdot(\vec{p}_3\times\vec{p}_1)}{4m^2}$$
$$\left.+\frac{i\vec{\sigma}_2\cdot(\vec{p}_4\times\vec{p}_2)}{4m^2}\right], \quad (18)$$

with the understanding that $\vec{p}_4=\vec{p}_1+\vec{p}_2-\vec{p}_3$. The first two correction terms are Darwin terms, and sum to $\pi\alpha/m^2\delta^3(\vec{r}_2-\vec{r}_1)$ in coordinate space. The last two are spin-orbit operators, which do not contribute to the S states considered here. We tabulate the Darwin terms in the second row of Table I.

Considering now Coulomb scattering between an electron and the nucleus, which we take to have charge Z although only $Z=2$ will be considered here, the nonrelativistic limit is given by

$$M_C{}^{e\text{-}N}(\vec{p}_3,\vec{p}_1) = -\frac{4\pi\alpha Z}{|\vec{p}_3-\vec{p}_1|^2} \quad (19)$$

with associated energy shift

$$E_C{}^{e\text{-}N} = -\frac{1}{(2\pi)^3}\int d^3p_1 d^3p_2 d^3p_3 \phi^*(\vec{p}_3,\vec{p}_2)$$
$$\times\frac{4\pi\alpha Z}{|\vec{p}_3-\vec{p}_1|^2}\phi(\vec{p}_1,\vec{p}_2). \quad (20)$$

Relativistic corrections are now obtained by introducing a Dirac spinor only for the electron (the nucleus is treated here in the infinite mass limit), and we find for exchange of a Coulomb photon

$$M_{DC}{}^{e\text{-}N}(\vec{p}_3,\vec{p}_1) = M_C{}^{e\text{-}N}(\vec{p}_3,\vec{p}_1)\left[1-\frac{|\vec{p}_3-\vec{p}_1|^2}{8m^2}\right.$$
$$\left.+\frac{i\vec{\sigma}_1\cdot(\vec{p}_3\times\vec{p}_1)}{4m^2}\right]. \quad (21)$$

Again only the Darwin term contributes for S states, but now corresponds to $\pi Z\alpha/m^2\delta^3(\vec{r}_1)$, which we tabulate in the third row of Table I.

The effect of transverse photon exchange between the electrons is simplified if we neglect retardation, which enters in order α^3 a.u., and in this approximation we have

$$M_{DT}{}^{e\text{-}e}(\vec{p}_3;\vec{p}_1,\vec{p}_2)$$
$$= \frac{\pi\alpha(p_3^2-p_1^2)(p_2^2-p_4^2)}{m^2q^4}-\frac{\pi\alpha}{m^2q^2}(\vec{p}_1+\vec{p}_3)\cdot(\vec{p}_2+\vec{p}_4)$$
$$-\frac{\pi\alpha}{m^2}(\vec{\sigma}_1\cdot\vec{\sigma}_2-\vec{\sigma}_1\cdot\hat{q}\vec{\sigma}_2\cdot\hat{q})-\frac{2\pi i\alpha}{m^2q^2}\vec{\sigma}_1\cdot(\vec{p}_2\times\vec{p}_4)$$
$$+\frac{2\pi i\alpha}{m^2q^2}\vec{\sigma}_2\cdot(\vec{p}_3\times\vec{p}_1), \quad (22)$$

where $q=|\vec{p}_3-\vec{p}_1|$. The first two terms, referred to as orbit-orbit terms or, following the notation of Bethe and Salpeter [16], as H_2, are usually evaluated by Fourier transforming into coordinate space. With the present approach, however, they are quite easily treated, and the result presented in the fourth row of Table I. The third term is another δ function, and the last terms again vanish for the S states considered here. The effect of transverse photon exchange for e-N scattering vanishes in the infinite nuclear mass limit used in this work.

The operators considered so far in this note have been studied for many decades, and have all been evaluated with much higher accuracy than presented here [17]. The utility of the present approach lies in the fact that operators that enter in higher order, generally derived in momentum space, are both fairly complicated when Fourier transformed to coordinate space, and in addition need to be evaluated with less accuracy than the terms treated above. We illustrate this point with relativistic corrections that contribute in order α^4 a.u. to S states. A complete set of operators for triplet states has been derived by Pachucki [18] using an effective-field theory approach, and we consider here the corrections to one-Coulomb photon exchange, Eq. (20) of that paper,

$$V_1 = \frac{4\pi\alpha}{q^2}\frac{1}{64m^4}\left[q^4 - \frac{4}{3}(\vec{p}_3 \times \vec{p}_1) \cdot (\vec{p}_4 \times \vec{p}_2)(\vec{\sigma}_1 \cdot \vec{\sigma}_2)\right.$$
$$\left. + \frac{5}{2}[(p_4^2 - p_2^2)^2 + (p_3^2 - p_1^2)^2] + 3q^2(p_1^2 + p_3^2 + p_2^2 + p_4^2)\right].$$

(23)

This expression corresponds to the next term in the p/m expansion in Eq. (18). While Ref. [18] treats triplet states, this particular result is also valid for the singlet case. We note that the last term vanishes for triplet states because of the symmetry $\phi(\vec{p}_1, \vec{p}_2) = -\phi(\vec{p}_2, \vec{p}_1)$ mentioned earlier, as also noted in Ref. [18]. The resulting energy shift of the $2\,^3S_1$ state is

$$E^{e\text{-}e} = -0.0062(2)\alpha^4 \text{ a.u.}$$

(24)

While again not of high accuracy, we note the extremely simple nature of the coding, which is almost identical to the program that evaluates the Darwin term. This contrasts with the more complicated coordinate space calculation, where numerous derivatives must be applied to wave functions, leading to a much lengthier expression. As with the $m\alpha^4$ corrections, much higher accuracy is available from working in coordinate space, with $-0.006\,344\,7\,\alpha^4$ a.u. the known result [19]. However, we note the momentum space accuracy corresponds to 3.7 kHz, to be compared with the experimental accuracy [20] of 60 kHz.

While the formula for V_1 given above is valid for singlet states, it gives a linearly divergent result in that case. It is quite simple, however, to regulate this divergence in momentum space, where one simply imposes the cutoff $|\vec{p}_i| < \Lambda$. An application of this momentum space regulator to the case of ground-state positronium hyperfine splitting can be found in Ref. [21]. In Table II we show results for the expectation

TABLE II. Expectation value of V_1 for the ground state of helium with the regulator $|\vec{p}_i| < \Lambda$ for different values of Λ. Units α^4 a.u. for $\langle V_1 \rangle$ and $m\alpha$ for Λ.

Λ	100	200	300
$\langle V_1 \rangle$	−26.9(1)	−59.4(4)	−90.9(6)

value of V_1 for the ground state of helium with different cutoffs Λ, with the linear dependence on Λ clearly visible. When combined with other linearly divergent terms in a complete calculation a Λ independent result will obtain in the limit of large Λ. By improving the accuracy found in this part of the calculation this procedure can be used to check the results of Ref. [3] without explicitly canceling the divergences: work on this problem is in progress.

II. CONCLUSIONS

We have presented the formula for the momentum space form of a powerful basis set for helium. While it has the potential for proving useful for scattering calculations on helium, we have concentrated on evaluating expectation values of operators that give relativistic and QED corrections to energy levels. Because these operators are derived in momentum space, this allows one to work entirely in momentum space. The next step in this research is the extension to states with nonvanishing angular momentum. The most important application we have in mind is to the fine structure of helium P states, where recent high-precision measurements by Hessels and co-workers [22] have the potential of allowing a determination of the fine-structure constant α to a precision of 4 ppb. Unfortunately, the present state of theory is unclear, where the most complete calculation by Drake [23], while consistent with the fine-structure interval ν_{01} measured in Ref. [22], is inconsistent with measurements of the interval ν_{12} [24,25]. This inconsistency has also been noted in Ref. [2]. It is possible that the relative simplicity of the method developed here can shed light on this situation.

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