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Calculations of properties of screened He-like systems using correlated wave functions

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The purpose of the present study is twofold. First, the techniques of correlated wave functions for two-electron systems have been extended to obtain results for *P* and *D* states in a screening environment, and in particular for Debye screening. In these calculations, the satisfaction of both the quantum virial theorem and a related sum rule has been enforced and found to provide a high degree of stability of the solutions. Second, in order to facilitate the general use of correlated wave functions in combination with sum rule stability criteria, a rather systematic computational approach to this notoriously cumbersome method has been developed and thoroughly discussed here. Accurate calculations for few-electron systems are of interest to plasma diagnostics; in particular, when inaccuracies in binding energies are drastically magnified as they occur in exponents of Boltzmann factors.

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I. INTRODUCTION

Prompted by the renewed interest in experimental studies of highly charged ions, atomic systems with few electrons have again become the focus of both theoretical and experimental investigations. Helium-like systems, in particular, are once more centerstage in a variety of different research projects. Parallel to this development in ion physics runs a complementary activity in the study of atomic processes in plasmas. Here too multiply ionized few-electron systems are of interest because the relative simplicity of their spectra renders them useful for plasma diagnostics. Furthermore, negative ions—predominantly the negative hydrogen ion-serve diagnostic purposes in astrophysical plasmas besides being an important agents of opacity.

The focus of much of modern atomic theory is on electron correlation in various systems and processes. This interest is shared by new developments in the physics of highly ionized systems, including clusters, and by studies of atomic systems in plasma environments. Two-electron systems, in particular, play an important role in this research because of the relative ease with which correlation effects can be identified and calculated. New aspects such as the need to include relativistic effects in highly charged ions, for instance, or the direct inclusion of screening potentials into atomic calculations [1,2] call for improved theoretical approaches. Correlated wave functions have the potential for such improvements.

The Debye-Hückel theory—although first formulated in the framework of the theory of electrolyte solutions [3]—is being widely used for the modeling of plasma screening [4] because it allows for an analytic treatment of the relevant integrals. The main shortcoming of the Debye model is its limitation to static screening.

The present research originated from previous work to include realistic, time-dependent screening potentials into atomic calculations *from the beginning* and, by doing so, calculate line broadening and the lowering of the continuum threshold simultaneously and on the same footing. While the time-dependent aspect is not our focus here, the need for screened wave functions of non-zero angular momenta for helium-like ions stimulated the present study which builds on the landmark article by Calais and Löwdin [5] in which the authors give an analytic expression for nested triple integrals of the type ‘‘exponential function times integer powers’’ in all three arguments. Correlated wavefunctions have been applied to screened *S*-states [12] and highly accurate results for correlated *P*-states have been given by Thakkar and Smith [6] though not for screened interactions.

II. PERIMETRIC COORDINATES

Correlated wave functions that depend explicitly on the interelectronic distance r_{12} are not commonly used in calculations of the correlation energy of two-particle systems, except in high-precision calculations for small atomic systems. Early two-electron approaches of this type are given in the landmark publications by Hylleraas [7] and Pekeris [8]. Applications to three-electron systems are much more recent [9]. For standard product wave functions, the interelectronic distance r_{12} enters the integrands only via the electronic repulsion term $1/r_{12}$ in the Hamiltonian and can be handled by the Legendre expansion. The calculation of the integrals with wave functions containing a correlation factor, i.e., a function of r_{12}, is a more difficult task because rather complicated functions of r_{12} may occur and because r_{12} becomes now a dynamical variable. The present work is mainly intended to provide tools to simplify the use of correlated wave functions.

The highlights of Calais and Löwdin's systematic study [5] of integrals containing functions of the radial coordinates r_1, r_2 as well as of the relative distance r_{12} as one of the dynamic integration variables are briefly reviewed here for completeness. We start with integrals of the type

$$\int f(r_1)g(r_2)h(r_{12})dv_1dv_2, \tag{1}$$

where f and g are spherically symmetric, and we treat the general case later [Eq. (8)]. Then we write

$$\begin{aligned}\int f(r_1)g(r_2)h(r_{12})dv_1dv_2\\ &=\int f(r_1)dv_1\int g(r_2)h(r_{12})dv_2\\ &=\int f(r_1)dv_1\frac{2\pi}{r_1}\int_0^\infty g(r_2)r_2dr_2\int_{|r_1-r_2|}^{r_1+r_2}h(r_{12})dr_{12}\\ &=8\pi^2\int_0^\infty f(r_1)r_1dr_1\int_0^\infty g(r_2)r_2dr_2\\ &\quad\times\int_{|r_1-r_2|}^{r_1+r_2}h(r_{12})r_{12}dr_{12}.\end{aligned}\tag{2}$$

The next step is the transformation of the integrands to perimetric coordinates defined by the following relations:

$$\begin{aligned}\rho&=-r_1+r_2+r_{12}, & r_1&=1/4(2\sigma+\tau),\\ \sigma&=r_1-r_2+r_{12}\quad\text{or} & r_2&=1/4(2\rho+\tau),\\ \tau&=2(r_1+r_2-r_{12}), & r_{12}&=1/2(\rho+\sigma),\end{aligned}\tag{3}$$

$$dr_1dr_2dr_{12}=1/8d\rho d\sigma d\tau.\tag{4}$$

With the following choice of functions:

$$f(r)=e^{-Ar}/r,\quad g(r)=e^{-Br}/r,\quad h(r)=e^{-Cr}/r,\tag{5}$$

the basic integral Eq. (1) is easily evaluated in the new coordinates because the limits of the three integrals become independent of each other. Compared to the direct calculation of the integrals this substitution brings a considerable simplification in that all integral limits extend from zero to infinity. The basic integral then becomes

$$\begin{aligned}8\pi^2\int_0^\infty e^{-Ar_1}dr_1\int_0^\infty e^{-Br_2}dr_2\int_{|\mathbf{r}_1-\mathbf{r}_2|}^{r_1+r_2}e^{-Cr_{12}}dr_{12}\\ &=\pi^2\int_0^\infty e^{-1/2\rho(B+C)}d\rho\int_0^\infty e^{-1/2\sigma(A+C)}d\sigma\\ &\quad\times\int_0^\infty e^{-1/4\tau(A+B)}d\tau\\ &=\frac{16\pi^2}{(A+B)(A+C)(B+C)}.\end{aligned}\tag{6}$$

More general integrals, containing various integer powers of r_1, r_2, and r_{12} can be obtained from this basic integral by taking appropriate derivatives with respect to the parameters A, B, and C.

The general analytic result for integer power functions of r_1, r_2, and r_{12} is given by

$$\begin{aligned}[K,L,M]\equiv\int_0^\infty dr_1r_1^Ke^{-Ar_1}\int_0^\infty dr_2r_2^Le^{-Br_2}\\ &\times\int_{|\mathbf{r}_1-\mathbf{r}_2|}^{r_1+r_2}dr_{12}r_{12}^Me^{-Cr_{12}}\\ &=2K!L!M!\sum_{p=0}^{K}\sum_{q=0}^{L}\sum_{r=0}^{M}\\ &\quad\times\frac{(p+q)!}{q!p!}\frac{(K-p+r)!}{r!(K-p)!}\frac{(L-q+M-r)!}{(M-r)!(L-q)!}\\ &\quad\times(A+B)^{-(p+q+1)}(A+C)^{-(K+1-p+r)}\\ &\quad\times(B+C)^{-(L+1-q+M-r)}.\end{aligned}\tag{7}$$

Computationally, this formula—whenever it can be applied—is advantageous over, for instance, the Gauss-Laguerre quadrature approach that has been presented earlier [10] by the present authors. In more general cases of interest, however, such a numerical formula can be useful by providing substantial convenience for programming. Furthermore, it can also be applied when the integrands contain functions which do not allow for analytic results. In these cases the numerical quadrature will no longer be exact but still of a high degree of accuracy.

Paraphrasing Calais and Löwdin [5] further, we turn now to the general atomic integral of the type

$$\begin{aligned}\int\int f(r_1)Y_{lm}(\Omega_1)h(r_{12})g(r_2)Y_{\lambda\mu}(\Omega_2)dv_1dv_2\\ &=2\pi(-1)^m\delta_{m,-\mu}\delta_{\lambda,l}Q_l(\zeta),\end{aligned}\tag{8}$$

where a function $Q_l(\zeta)$ has been defined as

$$\begin{aligned}Q_l(\zeta)=\int_0^\infty f(r_1)r_1^2dr_1\int_0^\infty g(r_2)r_2^2dr_2\int_0^\pi h(r_{12})\\ \times P_l(\cos\theta_{12})\sin\theta_{12}d\theta_{12},\end{aligned}\tag{9}$$

which, different from Calais and Löwdin, has been established with an index ζ to distinguish between different choices for the functions f, g, and h as they are used in the tables of the later sections.

Using the notation for more general integrands

$$\begin{aligned}(K,L,M)=\int_0^\infty f(r_1)r_1^Kdr_1\int_0^\infty g(r_2)r_2^Ldr_2\\ \times\int_{|r_1-r_2|}^{r_1+r_2}h(r_{12})r_{12}^Mdr_{12},\end{aligned}\tag{10}$$

the first three of the quantities $Q_l(\zeta)$ can be expressed as

$$Q_0(\zeta)=(1,1,1),\tag{11}$$

$$Q_1(\zeta)=\tfrac{1}{2}\{(2,0,1)+(0,2,1)-(0,0,3)\},\tag{12}$$

$$\begin{aligned}Q_2(\zeta)=\tfrac{3}{8}\{(3,-1,1)+(-1,3,1)+(-1,-1,5)+\tfrac{2}{3}(1,1,1)\\ -2(1,-1,3)-2(-1,1,3)\}.\end{aligned}\tag{13}$$

[Note: The factor $\frac{2}{3}$ in front of the fourth term of $Q_2(\zeta)$ has all the time been missing in Calais and Löwdin's original work [5].]

The angular functions in Eq. (9) are transformed into integer powers of the radial variables using the law of cosines

$$\cos\theta_{12} = \frac{r_1^2 + r_2^2 - r_{12}^2}{2r_1 r_2}, \tag{14}$$

the repeated application of which leads to the notoriously tedious expressions to calculate. The main goal of the present paper is to provide a set of tables with the help of which this procedure can be systematized to some degree.

III. THEORETICAL FOUNDATIONS

The nonrelativistic Hamiltonian for a two-electron atomic system with both electron-electron and electron-nucleus interactions screened is given by

$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{Z}{r_1}e^{-r_1/D} - \frac{Z}{r_2}e^{-r_2/D} + \frac{1}{r_{12}}e^{-r_{12}/D'}. \tag{15}$$

The denominator D' in the exponent of the last term facilitates the possibility of a different screening of the electron-electron interaction if the physical plasma model warrants this, although this option has not been used in the present study.

The eigenfunctions $|\Psi\rangle$ are defined in a state space spanned by a set of correlated and properly symmetrized functions $|abc\rangle$ as

$$|\Psi\rangle = \sum_{abc} f_{abc}|abc\rangle. \tag{16}$$

As an example, the following functional form has been chosen for *P*-state calculations:

$$|abc\rangle = (r_1 e^{-ar_1 - br_2}\cos\theta_1 + S_{pn} r_2 e^{-ar_2 - br_1}\cos\theta_2)e^{-cr_{12}}, \tag{17}$$

while

$$|abc\rangle = [r_1^2 e^{-ar_1 - br_2} P_2(\cos\theta_1) + S_{pn} r_2^2 e^{-ar_2 - br_1} P_2(\cos\theta_2)]e^{-cr_{12}} \tag{18}$$

is the choice for *D*-state calculations, where the sign parameter $S_{pn} = 1$ indicates singlet states and -1 triplet states.

Since the set of correlated basis functions $|abc\rangle$ is neither orthogonal nor normalized, the eigenvalue problem to solve is given by

$$\sum_{abc} f_{abc}(H_{a'b'c',abc} - ES_{a'b'c',abc}) = 0 \tag{19}$$

(for all combinations $a'b'c'$), where $S_{a'b'c',abc} = \langle a'b'c'|abc\rangle$ and $H_{a'b'c',abc} = \langle a'b'c'|\hat{H}|abc\rangle$.

TABLE I. Functions used in Eq. (20).

ζ	$f(x)$	$g(x)$	$h(x)$
1	$x^2 e^{-(a+a')x}$	$e^{-(b+b')x}$	$e^{-(c+c')x}$
2	$xe^{-(a+b')x}$	$xe^{-(a'+b)x}$	$e^{-(c+c')x}$
3	$xe^{-(a'+b)x}$	$xe^{-(a+b')x}$	$e^{-(c+c')x}$
4	$e^{-(b+b')x}$	$x^2 e^{-(a+a')x}$	$e^{-(c+c')x}$

IV. *P*-STATE CALCULATIONS

As computations of *S* states of screened two-electron systems with correlated wave functions of the same type have been reported relatively recently [2], the present paper will focus on higher angular momentum states (*P* and *D*).

The most basic integrals to be calculated are the elements of the overlap matrix. With the use of Eqs. (8)–(13), they are easily obtained (see Appendix A),

$$S_{a'b'c',abc} = \frac{8\pi^2}{3}[Q_0(1) + Q_0(4)] + S_{pn}\frac{8\pi^2}{3}[Q_1(2) + Q_1(3)]. \tag{20}$$

Table I represents different choices of the functions $f(x)$, $g(x)$, and $h(x)$ in $Q_l(\zeta)$.

The calculation of the elements of the Hamiltonian matrix for screened interactions, Eq. (15), requires more effort. The three potential-energy terms are readily obtained by a slight modification of Table I, replacing the function $f(x)$ by $f(x)\exp(-x/D)/x$,

$$\left\langle a'b'c' \middle| -\frac{Z}{r_1}e^{-r_1/D} \middle| abc \right\rangle = -Z\frac{8\pi^2}{3}[Q_0(1) + Q_0(4)] - S_{pn}Z\frac{8\pi^2}{3}[Q_1(2) + Q_1(3)]. \tag{21}$$

Similarly, the other parts can be calculated by replacing $g(x)$ with $g(x)\exp(-x/D)/x$ and $h(x)$ with $h(x)\exp(-x/D')/x$ in the original Table I, respectively.

TABLE II. Table I values modified for $\langle a'b'c'| -(Z/r_2)e^{-r_2/D}|abc\rangle$.

ζ	$f(x)$	new $g(x)$	$h(x)$
1	$x^2 e^{-(a+a')x}$	$\frac{1}{x}e^{-[b+b'+(1/D)]x}$	$e^{-(c+c')x}$
2	$xe^{-(a+b')x}$	$e^{-[a'+b+(1/D)]x}$	$e^{-(c+c')x}$
3	$xe^{-(a'+b)x}$	$e^{-[a+b'+(1/D)]x}$	$e^{-(c+c')x}$
4	$e^{-(b+b')x}$	$xe^{-[a+a'+(1/D)]x}$	$e^{-(c+c')x}$

As an example of such a modification of the original table, we turn to the matrix element $\langle a'b'c'|-(Z/r_2)e^{-r_2/D}|abc\rangle$, and show the modified table, Table II.

The final expression to compute is given by

$$\left\langle a'b'c'\left|-\frac{Z}{r_2}e^{-r_2/D}\right|abc\right\rangle = -Z\frac{8\pi^2}{3}[Q_0(1)+Q_0(4)] - S_{pn}Z\frac{8\pi^2}{3}[Q_1(2)+Q_1(3)]. \qquad (22)$$

To evaluate $Q_l(\zeta)$, the functions $f(x)$, $g(x)$, and $h(x)$ now have to be chosen from the ζth row of the modified table.

The calculation of the kinetic energy elements of the Hamiltonian matrix, variable transformation leads to a more involved expression,

$$\left\langle a'b'c'|-\tfrac{1}{2}(\nabla_1^2+\nabla_2^2)|abc\right\rangle = -\frac{4\pi^2}{3}\left[\sum_{\zeta=1}^{8} Q_0(\zeta)+Q_1(9)+\sum_{\zeta=10}^{17} Q_0(\zeta)+Q_1(18)\right] - \frac{4\pi^2}{3}S_{pn}\left[\sum_{\zeta=19}^{26} Q_1(\zeta)+Q_0(27) + \sum_{\zeta=28}^{35} Q_1(\zeta)+Q_0(36)\right], \qquad (23)$$

where the three functions are defined in Table III. The tables for the functions used to calculate the overlap and Hamiltonian matrices as well as Eqs. (8)–(13) provide the basis for a systematic way of computing the rest of the integrals needed to describe P states.

V. *D*-STATE CALCULATIONS

The elements of the overlap matrix are

$$S_{a'b'c',abc}=\frac{8\pi^2}{5}[Q_0(1)+Q_0(4)] + S_{pn}\frac{8\pi^2}{5}[Q_2(2)+Q_2(3)]. \qquad (24)$$

Here the functions $f(x)$, $g(x)$, and $h(x)$ in Eqs. (8)–(13) are defined in Table IV.

Similar to calculations of P states, we get

$$\left\langle a'b'c'\left|-\frac{Z}{r_1}e^{-r_1/D}\right|abc\right\rangle = -Z\frac{8\pi^2}{5}[Q_0(1)+Q_0(4)] - S_{pn}Z\frac{8\pi^2}{5}[Q_2(2)+Q_2(3)], \qquad (25)$$

where the three functions are almost the same as those in Table IV, except that the function $f(x)$ is replaced by $f(x)\exp(-x/D)/x$,

TABLE III. Three functions used in Eq. (23).

ζ	$f(x)e^{-(a+a')x}$	$g(x)e^{-(b+b')x}$	$h(x)e^{-(c+c')x}$
1	$x^2\left(a'^2+b'^2+c'^2-\frac{4a'}{x}\right)$	1	1
2	$-2b'x^2$	$1/x$	1
3	$-c'x^2(6-a'x)$	1	$1/x$
4	$b'c'x^2$	x	$1/x$
5	$-b'c'x^4$	$1/x$	$1/x$
6	$-a'c'x$	x^2	$1/x$
7	$b'c'x^2$	$1/x$	x
8	$a'c'x$	1	x
9	$2c'x$	x	$1/x$
ζ	$g(x)e^{-(a+a')x}$	$f(x)e^{-(b+b')x}$	$h(x)e^{-(c+c')x}$
10	$x^2\left(a'^2+b'^2+c'^2-\frac{4a'}{x}\right)$	1	1
11	$-2b'x^2$	$1/x$	1
12	$-c'x^2(6-a'x)$	1	$1/x$
13	$b'c'x^2$	x	$1/x$
14	$-b'c'x^4$	$1/x$	$1/x$
15	$-a'c'x$	x^2	$1/x$
16	$b'c'x^2$	$1/x$	x
17	$a'c'x$	1	x
18	$2c'x$	x	$1/x$
ζ	$f(x)e^{-(a'+b)x}$	$g(x)e^{-(a+b')x}$	$h(x)e^{-(c+c')x}$
19	$x\left(a'^2+b'^2+2c'^2-\frac{4a'}{x}\right)$	x	1
20	$-2b'x$	1	1
21	$-c'x(6-a'x)$	x	$1/x$
22	$b'c'x$	x^2	$1/x$
23	$-b'c'x^3$	1	$1/x$
24	$-a'c'$	x^3	$1/x$
24	$b'c'x$	1	x
26	$a'c'$	x	x
27	$2c'$	x^2	$1/x$
ζ	$g(x)e^{-(a'+b)x}$	$f(x)e^{-(a+b')x}$	$h(x)e^{-(c+c')x}$
28	$x\left(a'^2+b'^2+2c^2-\frac{4a'}{x}\right)$	x	1
29	$-2b'x$	1	1
30	$-c'x(6-a'x)$	x	$1/x$
31	$b'c'x$	x^2	$1/x$
32	$-b'c'x^3$	1	$1/x$
33	$-a'c'$	x^3	$1/x$
34	$b'c'x$	1	x
35	$a'c'$	x	x
36	$2c'$	x^2	$1/x$

TABLE IV. Functions used in Eq. (24).

ζ	$f(x)$	$g(x)$	$h(x)$
1	$x^4e^{-(a+a')x}$	$e^{-(b+b')x}$	$e^{-(c+c')x}$
2	$x^2e^{-(a+b')x}$	$x^2e^{-(a'+b)x}$	$e^{-(c+c')x}$
3	$x^2e^{-(a'+b)x}$	$x^2e^{-(a+b')x}$	$e^{-(c+c')x}$
4	$e^{-(b+b')x}$	$x^4e^{-(a+a')x}$	$e^{-(c+c')x}$

TABLE V. Three functions used in Eq. (28).

ζ	$f(x)e^{-(a+a')x}$	$g(x)e^{-(b+b')x}$	$h(x)e^{-(c+c')x}$
1	$x^4\left(a'^2+b'^2+2c'^2-\frac{6a'}{x}\right)$	1	1
2	$-2b'x^4$	$1/x$	1
3	$-c'x^4(8-a'x)$	1	$1/x$
4	$b'c'x^4$	x	$1/x$
5	$-b'c'x^6$	$1/x$	$1/x$
6	$-a'c'x^3$	x^2	$1/x$
7	$b'c'x^4$	$1/x$	x
8	$a'c'x^3$	1	x
9	$4c'x^3$	x	$1/x$
ζ	$g(x)e^{-(a+a')x}$	$f(x)e^{-(b+b')x}$	$h(x)e^{-(c+c')x}$
10	$x^4\left(a'^2+b'^2+2c'^2-\frac{6a'}{x}\right)$	1	1
11	$-2b'x^4$	$1/x$	1
12	$-c'x^4(8-a'x)$	1	$1/x$
13	$b'c'x^4$	x	$1/x$
14	$-b'c'x^6$	$1/x$	$1/x$
15	$-a'c'x^3$	x^2	$1/x$
16	$b'c'x^4$	$1/x$	x
17	$a'c'x^3$	1	x
18	$4c'x^3$	x	$1/x$
ζ	$f(x)e^{-(a'+b)x}$	$g(x)e^{-(a+b')x}$	$h(x)e^{-(c+c')x}$
19	$x^2\left(a'^2+b'^2+2c'^2-\frac{6a'}{x}\right)$	x^2	1
20	$-2b'x^2$	x	1
21	$-c'x^2(8-a'x)$	x^2	$1/x$
22	$b'c'x^2$	x^3	$1/x$
23	$-b'c'x^4$	x	$1/x$
24	$-a'c'x$	x^4	$1/x$
25	$b'c'x^2$	x	x
26	$a'c'x$	x^2	x
27	$4c'x$	x^3	$1/x$
ζ	$g(x)e^{-(a'+b)x}$	$f(x)e^{-(a+b')x}$	$h(x)e^{-(c+c')x}$
28	$x^2\left(a'^2+b'^2+2c'^2-\frac{6a'}{x}\right)$	x^2	1
29	$-2b'x^2$	x	1
30	$-c'x^2(8-a'x)$	x^2	$1/x$
31	$b'c'x^2$	x^3	$1/x$
32	$-b'c'x^4$	x	$1/x$
33	$-a'c'x$	x^4	$1/x$
34	$b'c'x^2$	x	x
35	$a'c'x$	x^2	x
36	$4c'x$	x^3	$1/x$

$$\left\langle a'b'c'\left|-\frac{Z}{r_2}e^{-r_2/D}\right|abc\right\rangle = -Z\frac{8\pi^2}{5}[Q_0(1)+Q_0(4)] - S_{pn}Z\frac{8\pi^2}{5}[Q_2(2)+Q_2(3)], \tag{26}$$

where the three functions are almost the same as those in Table IV, except that the function $g(x)$ is replaced by $g(x)\exp(-x/D)/x$,

$$\left\langle a'b'c'\left|\frac{1}{r_{12}}e^{-r_{12}/D'}\right|abc\right\rangle = \frac{8\pi^2}{5}[Q_0(1)+Q_0(4)]+S_{pn}\frac{8\pi^2}{5}[Q_1(2)+Q_1(3)] \tag{27}$$

with the function $h(x)$ replaced by $h(x)\exp(-x/D')/x$,

$$\left\langle a'b'c'\left|-\tfrac{1}{2}(\nabla_1^2+\nabla_2^2)\right|abc\right\rangle = -\frac{4\pi^2}{5}\left[\sum_{\zeta=1}^{8}Q_0(\zeta)+Q_1(9)+\sum_{\zeta=10}^{17}Q_0(\zeta)+Q_1(18)\right] - \frac{4\pi^2}{5}S_{pn}\left[\sum_{\zeta=19}^{26}Q_2(\zeta)+Q_1(27)+\sum_{\zeta=28}^{35}Q_2(\zeta) + Q_1(36)\right], \tag{28}$$

where the three functions are defined in Table V.

VI. SUM RULES

Sum rules have been introduced as stationarity conditions and goodness criteria into resonance calculations based on an expansion of dilatationally transformed Hamiltonians [12,13]. This technique is also called complex scaling and serves the purpose of determining complex variational wave functions when the usual criterion of energy minimization is not applicable. In the context of the present work which deals only with bound states and real-valued eigenvalues the use of sum rules is motivated rather by the need of optimizing a large number of exponents in the correlated basis functions. This nonlinear search is an addition to the usual linear optimization by the Ritz variational procedure and provides an alternative for the optimization of variational wave functions for excited states. In the present work, the number of nonlinear parameters is at least 56. This is prohibitively large for a full optimization. Instead, we scale three groups consisting of six parameters each independently. From these we form the required combinations.

The simultaneous satisfaction of the sum rules here, as in the complex case, enforces relevant properties that a meaningful wave function should exhibit. The first-order term of the energy expansion (not really a sum rule) is the quantum virial theorem, while the second-order term has the typical form of the sum occurring in perturbation theory of second order, and so on. The sum rule of the second order provides a stability condition.

We are studying He-like systems that experience screening modeled by Debye potentials

$$V=-\frac{Z}{r_1}e^{-r_1/D}-\frac{Z}{r_2}e^{-r_2/D}+\frac{1}{r_{12}}e^{-r_{12}/D'}. \tag{29}$$

Eigenfunctions $|\Psi\rangle$ are assumed in the form given in Eq. (16) with the correlated basis functions for *P* states as given in Eq. (17).

The satisfaction of the sum rules is expressed by the vanishing of the coefficients of the perturbation expansion. Explicitly, the first two conditions are the virial theorem

$$\left\langle \Psi \middle| 2T+i\left(\frac{\partial V}{\partial \theta}\right)_{\theta=0} \middle| \Psi \right\rangle=0, \tag{30}$$

and the sum rule of the second order

$$2T_{nn}-\frac{1}{2}\left(\frac{\partial^2 V}{\partial \theta^2}\right)_{\theta=0}-\sum_{b\neq n}\frac{\left\langle b \middle| 2T+i\left(\frac{\partial V}{\partial \theta}\right)_{\theta=0} \middle| n \right\rangle^2}{E_b-E_n}=0, \tag{31}$$

where

$$\left(\frac{\partial V}{\partial \theta}\right)_{\theta=0}=i\left[\frac{Ze^{-r_1/D}}{r_1}+\frac{Ze^{-r_2/D}}{r_2}-\frac{e^{-r_{12}/D'}}{r_{12}}+\frac{Ze^{-r_1/D}}{D}+\frac{Ze^{-r_2/D}}{D}-\frac{e^{-r_{12}/D'}}{D'}\right] \tag{32}$$

and

$$\left(\frac{\partial^2 V}{\partial \theta^2}\right)_{\theta=0}=\left[\frac{2Ze^{-r_1/D}}{D}+\frac{2Ze^{-r_2/D}}{D}-\frac{2e^{-r_{12}/D'}}{D'}\right]+\left[\frac{Ze^{-r_1/D}}{r_1}+\frac{Ze^{-r_2/D}}{r_2}-\frac{e^{-r_{12}/D'}}{r_{12}}\right]+\left[\frac{Zr_1e^{-r_1/D}}{D^2}+\frac{Zr_2e^{-r_2/D}}{D^2}-\frac{r_{12}e^{-r_{12}/D'}}{D'^2}\right]. \tag{33}$$

VII. NUMERICAL RESULTS

For a general two-electron atomic system described by the Hamiltonian

$$\hat{H}=\hat{T}_1+\hat{T}_2+V(r_1)+V(r_2)+W(r_{12}), \tag{34}$$

the quantum virial theorem (see, e.g., Ref. [11], p. 78) is given as

$$\langle[\hat{H},\hat{F}]_-\rangle=0 \tag{35}$$

with

$$\hat{F}=\frac{\hbar}{i}(\vec{r_1}\cdot\nabla_1+\vec{r_2}\cdot\nabla_2). \tag{36}$$

TABLE VI. (a) Triplet *P* states and (b) singlet *P* states.

D (a.u.)	E_1^{expt} (a.u.)	E_1^{theor} (a.u.)	S_a	S_b	S_c
		(a)			
2×10^6	−2.133 330	−2.133 083	1.11	1.665	5.03
200		−2.118 159	1.11	1.665	5.03
20		−1.990 202	1.11	1.665	4.83
2		−1.158 562	1.02	1.52	4.84
		(b)			
2×10^6	−2.124 002	−2.123 531	0.90	1.431	5.22
200		−2.108 613	0.90	1.431	5.22
20		−1.981 216	0.91	1.447	5.215
2		−1.157 886	1.02	1.622	5.207

Thus the application to the screened system corresponding to Eq. (15) leads to the virial theorem of the form

$$2\langle\hat{T}_1+\hat{T}_2\rangle=-\left\langle\left(1+\frac{r_1}{D}\right)V(r_1)+\left(1+\frac{r_2}{D}\right)V(r_2)+\left(1+\frac{r_{12}}{D'}\right)W(r_{12})\right\rangle. \tag{37}$$

Representative numerical results with wave functions of 56 terms are summarized in the following tables. S_a, S_b, and S_c are the dimensionless factors by which the constants *a*, *b*, and *c* in the wave functions of Eqs. (17) and (18) have been scaled, respectively.

Note that the Debye screening potential converges toward the Coulomb potential in the limit of weak screening, i.e., very large values of *D*. Tables VI(a) and VI(b) show that the numerical results reflect this fact well. For the lowest *P* states, our results compare well to highly accurate calculations by Thakkar and Vedene [4] (their values are −2.133 164 a.u. for the triplet and −2.123 843 a.u. for the singlet *P* states, respectively) as well as to experimental results [14] containing, naturally, all relativistic effects which are not included in the theoretical values. In the limit of strong screening, our results indicate that the energy levels of 2^1P and 2^3P tend to become closer. This is a reasonable result considering that with decreasing values of *D* the atomic system expands spatially [2], i.e., the two electrons stay further apart on the average. (See Table VII) S_a, S_b, and S_c are the dimensionless factors by which the constants *a*, *b*, and *c* in the wave functions of Eqs. (17) and (18) have been scaled, respectively.

TABLE VII. (a) Triplet D states and (b) singlet D states.

D (a.u.)	E_1^{expt} (a.u.)	E_1^{theor} (a.u.)	S_a	S_b	S_c
		(a)			
2×10^6	−2.055 808	−2.055 432	1.0	2.0	3.831
200		−2.040 578	1.0	2.0	3.830
50		−1.997 669	1.0	2.0	3.829
20		−1.918 472	1.0	2.0	3.805
10		−1.804 013	1.0	2.0	3.688
		(b)			
2×10^6	−2.055 793	−2.055 418	1.0	2.0	3.835
200		−2.040 566	1.0	2.0	3.835
50		−1.997 650	1.0	2.0	3.830
20		−1.918 423	1.0	2.0	3.796
10		−1.803 940	1.0	2.0	3.681

Enforcing the satisfaction of the virial theorem for an excited state provides an optimization criterion for the adjustment of the nonlinear parameters (see Sec. VIII). This is shown in Table VIII, where k indicates the particular state chosen for optimization. Note that only the kth state is optimized but not the lower states.

Again, S_a, S_b, and S_c are the dimensionless factors by which the constants a, b, and c in the wave functions of Eqs. (17) and (18) have been scaled, respectively.

VIII. AN EXAMPLE FOR THE USE OF THE TABLES

In this section we demonstrate via an example how a moderately complicated integral can be calculated using the tables presented above. Following this scheme, the computation of a large variety of integrals with various powers of r_1, r_2, and r_{12}, as well as with different exponents, can be significantly simplified.

We chose the integral $\langle\Psi'|(Zr_1e^{-r_1/D}/D^2)|\Psi\rangle$ which is one of the integrals necessary for the evaluation of the sum rules. First we notice that, aside from a constant factor Z/D^2, the integrand can be obtained by multiplying the integrand of the overlap matrix by $r_1e^{-r_1/D}$. Therefore Table I with some modifications can be used for the calculation of this particular integral.

Using Eqs. (8)–(13) we obtain

TABLE IX. This table is an example of a modification of an above given table, namely Table I, with the aim of accomodating a screening factor in one of the given functions. Here, $f(x)$ of Table I is modified by the factor $x\exp(-x/D)$ to represent a new function $f_{\text{new}}(x)$.

ζ	$f_{\text{new}}(x)$	$g(x)$	$h(x)$
1	$x^3e^{-[a+a'+(1/D)]x}$	$e^{-(b+b')x}$	$e^{-(c+c')x}$
2	$x^2e^{-[a+b'+(1/D)]x}$	$xe^{-(a'+b)x}$	$e^{-(c+c')x}$
3	$x^2e^{-[a'+b+(1/D)]x}$	$xe^{-(a+b')x}$	$e^{-(c+c')x}$
4	$xe^{-[b+b'+(1/D)]x}$	$x^2e^{-(a+a')x}$	$e^{-(c+c')x}$

$$\left\langle\Psi'\left|\frac{Zr_1e^{-r_1/D}}{D^2}\right|\Psi\right\rangle=\frac{Z}{D^2}\,\frac{8\pi^2}{3}[Q_0(1)+Q_0(4)+S_{pn}Q_1(2)+S_{pn}Q_1(3)], \quad (38)$$

where $g(x)$ and $h(x)$ are the same as those in Table I, while $f(x)$ is modified to account for the extra term $x\exp(-x/D)$. Table IX represents such modifications, and

$$f_{\text{new}}(x)=f(x)xe^{-x/D}. \quad (39)$$

To evaluate $Q_0(1)$ [see Eq. (11)], functions $f(x)$, $g(x)$, and $h(x)$ from the first row are chosen. Since the first function has now three extra powers of x (i.e., of r_1) without changes in the powers of r_2 or r_{12}, the integral (1, 1, 1) then becomes [4, 1, 1] with $A=a+a'+1/D$, $B=b+b'$, and $C=c+c'$. The term $Q_0(4)$ is computed similarly by picking functions from the fourth row. In this case, the integral (1, 1, 1) is modified into [2, 3, 1] with $A=b+b'+1/D$, $B=a+a'$, and $C=c+c'$. To evaluate $Q_1(2)$ [see Eq. (12)] three different integrals have to be evaluated using the functions from the second row. Integral (2, 0, 1) becomes [4, 1, 1], integral (0, 2, 1) is transformed into [2, 3, 1], and integral (0, 0, 3) changes to [2, 1, 3]. All three integrals have the exponential coefficients $A=a+b'+1/D$, $B=a'+b$, and $C=c+c'$. The same approach is used to evaluate $Q_1(3)$, choosing functions $f(x)$, $g(x)$, and $h(x)$ from the third row. Then integral (2, 0, 1) becomes [4, 1, 1] integral (0, 2, 1) changes to [2, 3, 1], and (0, 0, 3) is now [2, 1, 3]. All three integrals in this case have the same coefficients $A=a'+b+1/D$, $B=a+b'$, and $C=c+c'$. Integrals of the type [K, L, M] with known coefficients A, B, and C can be easily computed using the quadrature approach.

TABLE VIII. Different triplet D states with $D=2\times10^6$ a.u.

k	S_a	S_b	S_c	E_1 (a.u.)	E_2 (a.u.)	E_3 (a.u.)	E_4 (a.u.)	E_5 (a.u.)
1	1.0	2.0	3.831	−2.055 43				
2	1.0	2.0	3.7475	−2.055 20	−2.029 65			
3	1.0	2.0	3.873	−2.055 51	−2.030 54	−2.017 75		
4	1.0	2.0	3.9315	−2.055 57	−2.030 74	−2.018 23	−2.011 10	
5	1.0	2.0	3.68211	−2.054 92	−2.028 91	−2.013 83	−2.000 03	−1.977 54

IX. SUMMARY

Motivated by the importance of two-electron atoms and ions for plasma diagnostics, our main objective for this study was the development of a systematic approach for the use of correlated wave functions. This approach has been successfully developed, applied, and described in detail and is the major emphasis of this paper. While the present applications comprise the calculation of bound P and D state energies of the helium atom in a screening environment and are chosen to demonstrate the use of the quantum virial theorem and sum rule in second order, the numerical applications can be extended to include other heliumlike ions as well as the computation of other properties such as oscillator strengths and radial one-electron densities [2]. The computation of energies and lifetimes of autoionizing states, done so far only for the pure Coulomb potential [15], requires the analytic continuation onto the complex plane and has been the main motivation for the development of the sum rule criteria. The present studies will be extended into that area in the near future.

APPENDIX A

The overlap matrix for P states

$$S_{a'b'c',abc}=\langle a'b'c'|abc\rangle \tag{A1}$$

can be divided into four parts

$$S_{a'b'c',abc}=S_1+S_2+S_3+S_4, \tag{A2}$$

where

$$S_1=\int\int r_1^2 e^{-(a+a')r_1}e^{-(b+b')r_2}e^{-(c+c')r_{12}}\cos^2\theta_1 d\vec{r_1}d\vec{r_2},$$

$$S_2=\pm\int\int r_1r_2e^{-(a+b')r_1}e^{-(a'+b)r_2}e^{-(c+c')r_{12}}\times\cos\theta_1\cos\theta_2 d\vec{r_1}d\vec{r_2},$$

$$S_3=\pm\int\int r_1r_2e^{-(a'+b')r_1}e^{-(a+b')r_2}e^{-(c+c')r_{12}}\times\cos\theta_1\cos\theta_2 d\vec{r_1}d\vec{r_2},$$

$$S_4=\int\int r_2^2e^{-(a+a')r_1}e^{-(b+b')r_2}e^{-(c+c')r_{12}}\times\cos^2\theta_2 d\vec{r_1}d\vec{r_2}. \tag{A3}$$

It is easy to show that S_1 and S_4 can be represented by an integral of a type $Q_0=[0,0,0]$ with functions

$$f(r_1)=e^{-(a+a')r_1}r_1^2,\quad g(r_2)=e^{-(b+b')r_2},$$
$$h(r_{12})=e^{-(c+c')r_{12}}, \tag{A4a}$$

and

$$f(r_1)=e^{-(b+b')r_1},\quad g(r_2)=e^{-(a+a')r_2}r_2^2,$$
$$h(r_{12})=e^{-(c+c')r_{12}}, \tag{A4b}$$

respectively. Integrals S_2 and S_3 are of the type $Q_1=1/2\{(2,0,1)+(0,2,1)-(0,0,3)\}$ with functions

$$f(r_1)=e^{-(a+b')r_1}r_1,\quad g(r_2)=e^{-(a'+b)r_2}r_2,$$
$$h(r_{12})=e^{-(c+c')r_{12}} \tag{A5a}$$

and

$$f(r_1)=e^{-(a'+b)r_1}r_1,\quad g(r_2)=e^{-(a+b')r_2}r_2,$$
$$h(r_{12})=e^{-(c+c')r_{12}}, \tag{A5b}$$

respectively. Thus the simplified form of the overlap matrix is

$$S_{abc,a\ b\ c}=\sum_{n=1}^{4}S_n=\frac{8\pi^2}{3}[Q_0(1)+Q_0(4)]+S_{pn}\frac{8\pi^2}{3}[Q_1(2)+Q_1(3)], \tag{A6}$$

where S_{pn} represents ± for singlet and triplet states and numbers 1 through 4 represent different choices of functions in the integrals.

APPENDIX B

One of the authors (P.W.) would like to correct a long-standing faulty formula: Eq. (25) of Ref. [16] should read as follows:

$$\hat{H}\varphi=\Bigg(-\frac{a^2+b^2+2c^2}{2}+\frac{a-2}{r_1}+\frac{b-2}{r_2}+\frac{2c+1}{r_{12}}-ac\frac{r_1}{2r_{12}}-bc\frac{r_2}{2r_{12}}-bc\frac{r_{12}}{2r_2}-ac\frac{r_{12}}{2r_1}+bc\frac{r_1^2}{2r_2r_{12}}+ac\frac{r_2^2}{2r_1r_{12}}\Bigg)\times e^{-ar_1}e^{-br_2}e^{-cr_{12}}\pm\Bigg(-\frac{a^2+b^2+2c^2}{2}+\frac{b-2}{r_1}+\frac{a-2}{r_2}+\frac{2c+1}{r_{12}}-bc\frac{r_1}{2r_{12}}-ac\frac{r_2}{2r_{12}}-ac\frac{r_{12}}{2r_2}-bc\frac{r_{12}}{2r_1}+ac\frac{r_1^2}{2r_2r_{12}}+bc\frac{r_2^2}{2r_1r_{12}}\Bigg)e^{-br_1}e^{-ar_2}e^{-cr_{12}}. \tag{B1}$$

Here a, b, c stand for the corresponding Greek letters α, β, γ in the earlier reference. The results of Ref. [16] were obtained using the correct expressions.

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