Radial Configurational Interaction in Helium and Similar Atomic Systems

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The spherically symmetric component of the ground-state wave functions of the two-electron series (H^-, He, Li^+, Be^{2+}, C^{4+}, O^{6+}, and Ne^{8+}) has been investigated by using the orthonormal complete set of $(2q+2)$-order associated Laguerre functions as radial orbitals in the method of superposition of configurations. The results for the total energies and the corresponding expansion coefficients demonstrate the excellent convergence properties of these functions. They are also useful practically since only one single-orbital exponent is used. Applied to excited quantum states, they indicate a more slowly convergent process.

THE method of superposition of configurations has already been applied to the problem of the ground state of helium by several authors.[1–4] Recent investigations by Löwdin and Shull[4] show the necessity of including continuum terms in the hydrogen-like set of functions when rapid convergence is sought. However, by using the orthogonal complete set of associated Laguerre functions (applied first to helium by Hylleraas[1]), we can avoid such an inclusion. It is surprising to see how much less attention has been paid in the literature to this complete set of functions than to the hydrogen-like set when an atomic or molecular wave function is built up as an expansion in configurations. They also have been applied in a modified form, including radial configurational interaction only,[5,6] to the problem of non-spherically-symmetric states.

The results presented in this short note are the first step in the development of a systematic, practical procedure for obtaining a configurational wave function (with rapid convergence) for any spherically symmetric state of a many-electron system in terms of normalized Legendre functions of the cosine of the angles which the electrons subtend at the nucleus.

The calculations were based on the following configurational expansion of the wave function:

$$\Psi(r_1,r_2,r_{12})=\sum_{m,n,q} c(mq|nq)\,\varphi^N(mq|\eta r_1)\times\varphi^N(nq|\eta r_2)P_q{}^N(\cos\vartheta),$$

where the $P_q{}^N(\cos\vartheta)$ are the normalized Legendre polynomials of order q of the cosine of the angle between the electron vectors, and the $\varphi^N(nq|\eta r)$ are the orthonormal complete set of radial orbitals[7]:

$$\varphi^N(nq|\eta r)=-N(n,q)(2\eta r)^q L_{n+q+1}{}^{2q+2}(2\eta r)\times\exp(-\eta r)/(n+q+1)!$$
$$=(2\pi i)^{-1}N(n,q)\int_C dt\times(2\eta r)^q t^{-n+q}(1-t)^{-2q-3}\times\exp\left(-\frac{\eta(1+t)r}{1-t}\right).$$

Here the $(2\eta r)^q L_{n+q+1}{}^{2q+2}(2\eta r)\times\exp(-\eta r)$ are the associated Laguerre functions of order $2q+2$, n and q are the principal and azimuthal quantum numbers, respectively, of the configurations included, and η is the effective nuclear charge (the scale constant). By using positive integral values of n and q only, as required in these computations, the path of integration C of the above contour integral is reduced to a closed curve enclosing the singular point $t=0$.

By means of an electrical computer it has been possible to calculate the total energies and the corresponding expansion coefficients of the spherically-symmetric component ($q=0$) for the ground states of helium and similar atomic systems up to neon. The inclusion of the terms (configurations) in the wave function can be made in different ways. As a result of later investigations on three- and four-electron systems, the sequence shown in Table I has been chosen. As can be seen from Table I, the data show a surprisingly rapid convergence for all the members of the series isoelectronic with helium, with the exception of the negative hydrogen ion. However, by the addition of successive configurational terms (up to $6s^2$) we have shown that here also the energy converges towards a finite limit, listed in Table II. As would be expected, the total energies calculated for helium (listed in Table I in parentheses) agree pretty well with those obtained by Löwdin and Shull[4] in their natural-orbitals expansion of rank 2, 3, and 4. The data presented in Table II emphasize especially the excellent approximation of the very simple symmetrized exponentials $e^{-\eta(1+\gamma)r_1-\eta(1-\gamma)r_2}+e^{-\eta(1-\gamma)r_1-\eta(1+\gamma)r_2}$, where η is the scale constant and γ is a splitting parameter, but also demonstrate the good agreement between our results and those estimated by Green *et al.*[3] As can be seen from Table III, the process

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TABLE I. The expansion coefficients of the spherically symmetric component of the ground-state wave functions. $c(1s^2)=1$. Total energies ($-Z^{-2}E$) in units of R_Zhc are given in parentheses.

Atoms	Superposed configurations		
	$1s^2$, $1s2s$, $2s^2$	$1s^2$, $1s2s$, $2s^2$, $1s3s$, $2s3s$, $3s^2$	$1s^2$, $1s2s$, $2s^2$, $1s3s$, $2s3s$, $3s^2$, $1s4s$, $2s4s$, $3s4s$, $4s^2$
H^-	$\eta=1$ −0.04753, −0.45946 (0.92768) $\eta=0.6875$ −0.02527, −0.16785 (0.97416)	$\eta=1$ −0.77492, −0.04385, +0.36320, +0.00351, −0.01018 (1.00417) $\eta=0.6875$ −0.31117, −0.23145, +0.38676, −0.00003, +0.01223 (1.02488)	$\eta=1$ −0.86789, −0.04314, +0.58846, −0.00370, −0.00702, −0.18401, +0.01178, −0.00158, −0.00396 (1.01848) $\eta=0.6875$ −0.33465, −0.23781, +0.43317, +0.02703, +0.01812, −0.03226, −0.03698, −0.00624, −0.00666 (1.02604)
He	$\eta=2$ −0.25354, −0.03495 (1.42511) $\eta=1.6875$ −0.00385, −0.06045 (1.43020)	$\eta=2$ −0.36761, −0.03386, +0.13539, −0.00046, −0.00695 (1.43906) $\eta=1.6875$ −0.08566, −0.06488, +0.11238, −0.00701, −0.00675 (1.43863)	$\eta=2$ −0.37040, −0.03423, +0.14659, −0.00504, −0.00507, −0.01113, +0.00758, −0.00225, −0.002753 (1.43930) $\eta=1.6875$ −0.08042, −0.06418, +0.09035, −0.01154, −0.00532, +0.02406, +0.00615, −0.00388, −0.00332 (1.43918)
Li^+	$\eta=3$ −0.17367, −0.02598 (1.60639) $\eta=2.6875$ −0.00148, −0.03678 (1.60778)	$\eta=3$ −0.23621, −0.02504, +0.07722, −0.00166, −0.00504 (1.61146) $\eta=2.6875$ −0.048239, −0.037361, +0.064934, −0.005182, −0.00529 (1.61117)	$\eta=3$ −0.23542, −0.025350, +0.07391, −0.004766, −0.00367, +0.00348, +0.00531, −0.00190, −0.00201 (1.61156) $\eta=2.6875$ −0.04603, −0.03733, +0.05046, −0.00831, −0.00404, +0.01685, +0.00495, −0.00270, −0.00230 (1.61150)
Be^{2+}	$\eta=4$ −0.13180, −0.02049 (1.70067) $\eta=3.6875$ −0.00078, −0.02642 (1.70123)	$\eta=4$ −0.17353, −0.01964, +0.05292, −0.00187, −0.00393 (1.70320) $\eta=3.6875$ −0.03346, −0.02633, +0.04562, −0.00400, −0.00414 (1.70305)	$\eta=4$ −0.17267, −0.01990, +0.04773, −0.00418, −0.00286, +0.00579, +0.00404, −0.00158, −0.00158 (1.70329) $\eta=3.6875$ −0.03227, −0.02632, +0.03503, −0.00630, −0.00313, +0.01269, +0.00387, −0.00205, −0.00175 (1.70326)
C^{4+}	$\eta=6$ −0.08878, −0.01433 (1.79760) $\eta=5.6875$ −0.00032, −0.01690 (1.79776)	$\eta=6$ −0.11320, −0.01364, +0.03197, −0.00171, −0.00272 (1.79859) $\eta=5.6875$ −0.02071, −0.016424, +0.028592, −0.00272, −0.00284 (1.79854)	$\eta=6$ −0.11269, −0.01384, +0.02718, −0.00322, −0.00199, +0.00562, +0.00272, −0.00116, −0.00110 (1.79865) $\eta=5.6875$ −0.02021, −0.01656, +0.02175, −0.00421, −0.00212, +0.00842, +0.00265, −0.00138, −0.00118 (1.79864)
O^{6+}	$\eta=8$ −0.06689, −0.01099 (1.84711) $\eta=7.6875$ −0.00017, −0.01242 (1.84717)	$\eta=8$ −0.08395, −0.01043, +0.02274, −0.00147, −0.00208 (1.84763) $\eta=7.6875$ −0.01499, −0.01196, +0.02081, −0.00205, −0.00215 (1.84760)	$\eta=8$ −0.08365, −0.01058, +0.01877, −0.00258, −0.00152, +0.00479, +0.00204, −0.00091, −0.00084 (1.84767) $\eta=7.6875$ −0.01471, −0.01208, +0.01577, −0.00315, −0.00160, +0.00629, +0.00200, −0.00104, −0.00089 (1.84766)
Ne^{8+}	$\eta=10$ −0.05365, −0.00891 (1.87716) $\eta=9.6875$ −0.00011, −0.00982 (1.87719)	$\eta=10$ −0.06673, −0.00843, +0.01761, −0.00127, −0.00168 (1.87747) $\eta=9.6875$ −0.01174, −0.00940, +0.01637, −0.00165, −0.00173 (1.87746)	$\eta=10$ −0.06651, −0.00856, +0.01427, −0.00215, −0.00123, +0.00408, +0.00163, −0.00075, −0.00068 (1.87750) $\eta=9.6875$ −0.01157, −0.00951, +0.01237, −0.00252, −0.00128, +0.00502, +0.00161, −0.00083, −0.00071 (1.87750)

TABLE II. The radial limit of the total energies ($-Z^{-2}E$) in units of $R_Z hc$ when maximum of configurations are included.

Atoms	Radial limits	Symmetrized exponentials	Estimated maximum and minimum[a]
H^-	1.0262	1.0266	1.0231, 1.0264
He	1.4394	1.4378	1.4388, 1.4400
Li^+	1.6116	1.6108	1.6114, 1.6121
Be^{2+}	1.7034	1.7029	
C^{4+}	1.7986	1.7985	
O^{6+}	1.84767	1.84756	
Ne^{8+}	1.87750	1.87744	

[a] From Green *et al.*, see reference 3.

applied to excited quantum states (here the doubly excited state) shows a slower energy convergence, but

TABLE III. Doubly excited $(2s^2)\ ^1S$ state of helium. Total energies obtained by similar approximations. $\eta=0.5$, $c(2s^2)=1$.

Terms up to $2s^2$	Terms up to $3s^2$	Terms up to $4s^2$
0.3494	0.3566	0.3626

the best total energy calculated for the doubly excited state $(2s^2)\ ^1S$ of helium ($-1.4504\ R_{He}hc$, terms up to $4s^2$, $\eta=0.5$) is lower than the Hartree-Fock energy ($-1.4404\ R_{He}hc$).

Investigations on the angular component ($q=1, 2, 3$, etc.) are now in progress and fuller details of the calculations will be given elsewhere.

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Scattering of 7.5-Mev Protons by Helium*

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The differential cross section for the elastic scattering of 7.5±0.1 Mev protons from helium has been measured at 2.5° intervals over the laboratory angular range 10° to 172.5° using the Los Alamos nuclear plate camera. The results obtained have an absolute standard error of ±2.5% to ±3%. A phase-shift analysis of the data gives for the S, P, and D phase shifts: $\delta_0=-57.95°$, $\delta_1{}^+=112.1°$, $\delta_1{}^-=52.51°$, $\delta_2{}^+=0.44°$, $\delta_2{}^-=-1.87°$. These results fit the experimental data with a root-mean-square deviation of 2.7% and appear to be in harmony with those determined from experiments at other energies.

I. INTRODUCTION

THE general theoretical interest in the interactions of the hydrogen and helium isotopes has prompted many experimental studies over a wide range of energies. In spite of this there still exist many gaps in the data. The new Los Alamos variable-energy cyclotron facilitates the closing of these gaps in the region of moderate energies.

Previous measurements on the proton helium interaction have been made at 0.95 to 3.58 Mev,[1] 5.10 Mev,[2] 5.78 Mev,[3] 9.48 Mev,[4] 9.55 Mev,[5] 9.73 Mev,[6] 9.76 Mev,[7] 17.5 Mev,[8] and 31.6 Mev.[9] Theoretical treatments in terms of phase-shift analysis have been done by Critchfield and Dodder[10] on the work of Freier *et al.*; by Dodder and Gammel[11] on the measurements of Kreger *et al.* and Putnam. The phase shifts have been treated, in terms of a potential interaction between the proton and alpha-particle core with a spin-orbit interaction of the Thomas type, by Sack *et al.*[12] An interpretation in terms of the energy levels of the compound nucleus Li^5 has been given by Adair.[13]

Examination of the available data indicated that in order to firmly establish the variation of the phase shifts with energy, in the energy region below 10 Mev, a measurement at about 7.5 Mev would be highly beneficial.

II. EXPERIMENTAL APPARATUS AND PROCEDURE

The nuclear multiplate camera used in this measurement has been described in detail elsewhere.[14] Certain modifications have been made, however, to reduce the background of slit and collimator scattered particles and to improve, in general, the data obtained. These modifications together with the experimental setup associated with the Los Alamos variable-energy cyclotron will now be described.

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