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Hylleraas-Type Calculations of the Be Ground State

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Results of low-order Hylleraas-type calculations of the Be ground state are given for expansions of 1–18 terms. The 18-term expansion gives an energy of − 14.6611 a.u., which is slightly better than results of a 25-term Hylleraas-type calculation by Gentner and Burke and is comparable to the 55-term configuration-interaction result of Weiss: it is substantially poorer than results of recent much more extensive calculations by Bunge and by Sims and Hagstrom. A brief discussion is given of the additivity properties of energy contributions from expansion terms contributing to various types of correlation effects and of the relative importance, in the inner and outer shells separately, of various types of correlation effects.

INTRODUCTION

There are two principal means of accounting for electron correlation effects in Rayleigh-Ritz variational calculations of atomic structure. The configuration-interaction (CI) method is based on products of one-electron functions, while the Hylleraas[1] method involves correlation factors of the form r^p_{ij}. (This is sometimes referred to as the r^p_{ij}-type method.) The latter method, which is of primary interest herein, has been used to obtain a phenomenal precision for two-electron atoms. Coolidge and James[2] extended the method to three-electron atoms; they also gave formulas[3] which are very useful in evaluating the required three-electron integrals and which can be readily extended to four-electron problems. A 100-term calculation of the Li ground state was performed by Larsson.[4] We have recently carried out low-order calculations for some excited S states in Li.[5]

There have been a few Hylleraas-type calculations for four-electron systems, dealing with the beryllium ground state. Szasz and Byrne[6] carried out a calculation of this general type (with some special features) and obtained an energy lying about 0.01 a.u. (1 a.u.=2 Ry) above the experimental value. Gentner and Burke[7] used a 25-term expansion to obtain an energy about 0.008 a.u. above experiment. The present paper reports results obtained with a different choice of expansion terms. To date, all Hylleraas-type calculations (including the present one) for four-electron atoms have been subject to the restriction of at most one r^p_{ij} correlation factor per expansion term. It is clear from Larsson's work[4] that this restriction is not important for three-electron atoms, but the situation may well be different for four electrons.

The Be ground state has also been calculated with the CI method. Until fairly recently, the best variational results for this state were the 55-term CI results of Weiss.[8] Bunge[9] has subsequently reported a 180-term CI calculation of this state.

Recently, Sims and Hagstrom[10] (SH) have reported a calculation which combines features of CI and Hylleraas-type methods. The SH approach is an especially favorable one, since r_{ij}-type correlation is important in the inner shell, while angular correlation of the $2p^2$ sort is important in the outer shell. This fact was already clear from the excellent results obtained by SH; it is also verified in the present work, in which we test various combinations of terms, some of which are equivalent to employing angular correlation in the outer shell. The present results are not nearly so good as those from the much more extensive calculations of SH, which are very near the experimental value. The present results, however, are apparently the best available ones for expansions of 18 terms or less and hence may be useful in other calculations in which one wishes to utilize moderately short expansions.

METHOD

In treating a four-electron state with $M_S=0$, it suffices to deal with the spatial function which multiplies a particular one of the possible spin functions. We arbitrarily choose the ↑↓↑↓ spin function, and hence explicitly antisymmetrize on $\underline{r}_1$, $\underline{r}_3$ and on $\underline{r}_2$, $\underline{r}_4$. Prior to application of the Pauli-principle antisymmetrizers, we make each term of the trial function symmetric in $\underline{r}_1$, $\underline{r}_2$, which can be roughly described as corresponding to a singlet-core state; similarly, we make each trial function term symmetric (or antisymmetric) in $\underline{r}_3$, $\underline{r}_4$ so as to obtain an over-all singlet (or triplet) state. The singlet-core designation is only qualitative, and the permutation-symmetry operations just mentioned do not preclude incorporation of all types of spin-coupled states in the overall trial function.[8]

Each term of the trial function is a product of Slater-type orbitals and at most one correlation factor of the form r^p_{ij}, where p is a positive integer and the particular pair of subscripts i and j can be arbitrarily chosen. The trial function can then be written as

$$\phi_s = r_1^k r_2^m r_3^n r_4^r r^p_{ij} e^{-\alpha r_1 - \beta r_2 - \gamma r_3 - \delta r_4}, \tag{1}$$

$$\psi_s = [(1 - P_{13})(1 - P_{24})]\,(1 + P_{12})(1 \pm P_{34})\phi_s, \tag{2}$$

$$\psi = \sum_s C_s\,\psi_s\,. \tag{3}$$

The symmetry operations $1 + P_{12}$ and $1 + P_{34}$ are not explicitly applied to expansion terms for which they would be superfluous. It is a straightforward matter to express the matrix elements of H as sums of four-electron integrals. Because of the restriction to at most one correlation factor per expansion term, each integral will involve at most three factors of the form r^p_{ij}.

The methods used for evaluating the integrals will be only briefly outlined. These fall into two categories, depending on whether the interelectronic distances in the integrand involve all four electrons. If they do not, the four-electron integral is written as a product of a trivial one-electron integral and a three-electron integral. The latter is evaluated by expressions given previously[11] and by use of James-Coolidge[3] recursion formulas for the auxiliary functions which arise. In a certain exceptional case, we use a series-summation formula of Öhrn and Nordling[12] in lieu of recursion formulas.

If the integrand contains interelectronic distances involving all four electrons, we make use of explicit formulas given earlier[13] for the two types of integrals which arise; these are labeled K and L integrals and are defined by Eqs. (3) and (4) of a previous paper.[13] The special form of the K and L integrals, and the relative ease with which they can be evaluated, results from the present restriction of at most one r^p_{ij} correlation factor per expansion term. If this restriction is dropped, more complicated types of integrals arise. These can be evaluated by summing over the 24 permutations of the four variables and employing four-electron auxiliary functions analogous to the James-Coolidge[3] three-electron auxiliary function W.

All integrals are evaluated by essentially algebraic, as distinguished from numerical-integration, methods.

Matrix elements of H and unity were calculated in single-precision (essentially eight-decimal) arithmetic on an IBM-7094 computer and were punched into cards. These cards were then used as input to an IBM-1620, which was used to solve the secular equation for the lowest eigenvalue and the corresponding expansion coefficients. This two-phase mode of operation is cumbersome but is convenient for testing various combinations of expansion terms (for relatively short expansions), since various groupings of terms can be obtained by simply hand sorting the matrix-element cards (consistency of ordering is checked by the computer program). Among the checks for proper operation of the computer programs was the reproduction of the energies obtained by Gentner and Burke[7] with expansion lengths of from one to eight terms.

RESULTS

For most of the expansion terms, as indicated in Table I, exponential parameters of 3.70 and 0.96 were used for the inner and outer shells, respectively. This choice was originally based on the results of Morse, Young, and Haurwitz,[14] and was found to be near optimum for a five-term expansion. The two expansion terms which are marked with asterisks in Table I were included to correspond to a contribution to the 2s orbital

TABLE I. Expansion parameters and calculated energies for Be $1s^2\,2s^2\,{}^1S$. Column headings are subscripts i and ij of the arguments r_i and r_{ij}, and entries in each column are the powers of the corresponding arguments. For all terms, $\alpha = \beta = 3.70$. For all terms not marked with an asterisk, the value of $\gamma = \delta = 0.96$. For the terms marked with an asterisk, the value of γ or δ associated with the zeroth power of the corresponding r_i is 3.15. The essentially exact energy calculated from experiments is −14.667 a.u.

Term No.	1	2	3	4	12	13	14	23	24	34	$-E$ (a.u.)
1	0	0	1	1	0	0	0	0	0	0	14.5565
2	0	0	1	1	1	0	0	0	0	0	14.5881
3	0	0	0	0	0	0	0	0	0	2	14.6109
4	0	0	2	0	0	0	0	0	0	0	14.6280
5	1	1	1	1	0	0	0	0	0	0	14.6436
6	0	0	1	0*	0	0	0	0	0	0	14.6463
7	0	0	0*	0*	0	0	0	0	0	0	14.6464
8	2	0	1	1	0	0	0	0	0	0	14.6492
9	0	0	0	0	0	0	0	0	0	1	14.6510
10	1	0	1	1	0	0	0	0	0	0	14.6528
11	0	0	1	1	2	0	0	0	0	0	14.6552
12	0	0	1	0	0	0	1	0	0	0	14.6580
13	0	0	1	0	0	0	2	0	0	0	14.6591
14	1	1	0	0	0	0	0	0	0	2	14.6592
15	2	0	0	0	0	0	0	0	0	2	14.6607
16	1	1	2	0	0	0	0	0	0	0	14.6608
17	2	0	2	0	0	0	0	0	0	0	14.6611
18	0	0	2	0	1	0	0	0	0	0	14.6611

used by Morse, Young, and Haurwitz.[14]

The ordering of terms in Table I was mostly obtained by searching for the terms which, when added to a set of given terms, gave the largest energy contribution. Attempts were made to find choices of expansion terms which converged rapidly, but we were not successful in finding any really clever choice. One idea that was tested was the use of split-inner-shell terms, i.e., terms with different exponential parameters for the two inner electrons. This led to some improvement in energy at very low order, but the improvement quickly washed out when further terms were included. Numerous terms in addition to those listed in Table I were tested and rejected. Each prospective term was tested by simply noting its effect on energy when added to a relatively small number of other terms. Because this testing was done in low order and in a not particularly systematic way, and because of nonadditivity of energy contributions, it may well be that some of the terms which were discarded in the present work would make substantial contributions in a more extensive calculation.

Some rough qualitative conclusions can be reached regarding the energy contributions of various types of expansion terms in various combinations. These conclusions are rather tentative, in view of the limited number of expansion terms used here and the fact that, owing to the simple analytic form of the orbitals used here, the present one-term energy (–14.5565 a.u.) is somewhat poorer than the best possible one-term result, i.e., the Hartree-Fock result (–14.5730 a.u.).[15] The question of additivity of effects of two terms or groups of terms is of particular interest. In general, effects are not additive. Two situations are of interest, namely, additivity of groups of terms which separately contribute to correlation within each of the two shells and additivity of terms contributing to correlation within one shell.

Certain types of calculations[16] depend on the assumption that, to a high degree of approximation, the over-all correlation energy can be expressed as a sum of pair correlation energies. For the Be ground state, this implies additivity of inner- and outer-shell correlation energies (each being of the order of 0.04 a.u.) and an intershell correlation energy (of the order of 0.006 a.u.).[16] We find that the inner-shell correlation terms 2, 5, 8, and 11 contribute about 10% less to the correlation energy when the outer-shell correlation terms 3 and 4 (as well as term 1) have been included than they do when terms 3 and 4 are omitted; a similar statement holds when one considers only subsets of terms 2, 5, 8, and 11. Similarly, the outer-shell correlation terms 3 and 4 contribute about 10% less when the inner-shell correlation terms 2, 5, 8, and 11 (as well as term 1) have been included than they do when only term 1 is included. The estimate for the over-all correlation energy obtained with the terms just listed is roughly 5% less than one would obtain by adding the separate estimates of the inner- and outer-shell correlation energies. (A related comparison by Szasz and Byrne[6] indicated a nonadditivity of about 4%.)

In some cases there is a pronounced nonadditivity of effects of terms contributing to correlation within one of the shells, when terms contributing to correlation in the other shell are held fixed. The sum of the separate energy contributions from the inner-shell radial-correlation terms 5 and 8, when added to the basic term 1, is less than one-fourth as large as the contribution when both terms are added. However, when the basic expansion is taken to be terms 1 and 2, the separate contribution of term 5 becomes much larger and the effects of terms 5 and 8 are roughly additive. The above statements also hold when the outer-shell correlation terms 3 and 4 are included in the basic expansion.

The nonadditivity of the outer-shell correlation terms 3 and 4 is very pronounced; the radial-correlation term 4 makes a very small contribution, term 3 makes a large contribution, and the contribution from the combination of 3 and 4 is considerably larger still. These statements hold when the basic expansion which is held fixed is merely term 1 or various combinations involving the inner-shell correlation terms mentioned above.

In a very rough way, one can consider the relative importance of terms contributing within a particular shell to what we may call radial, angular, and r_{ij} effects. (The latter effect will be understood to correspond to odd values of the integer p in the factor r^p_{ij}.) Note that, by the cosine formula a combination of terms 1, 3, and 4 can contribute to a $2p^2$ type of angular dependence in the outer shell, while a combination of terms 1, 8, and 11 can contribute this sort of angular dependence in the inner shell. The aforementioned fact that the contribution of term 4 alone is very small while the combination of 3 and 4 (in combination with the basic term 1) is large indicates that there is a large $2p^2$ contribution in the outer shell; this would be expected in view of the near degeneracy with $2s^2$.[17] A few terms involving the first power of the correlation factor r_{34} were tested. Energy contributions from some of these terms are substantial when terms 3 and 4 are not also included, but are much smaller when 3 and 4 have been included. It appears that outer-shell correlation is more closely related to a $2p^2$ angular dependence than to a dependence arising from an odd power of r_{34}. The present independent study thus suggests the desirability of a combined CI and r_{ij} approach, or its equivalent. That such an approach does work very well indeed was of course already demonstrated by the excellent results obtained by Sims and Hagstrom.[10]

In the inner shell, there is a very large contribution from term 2, which contains the first power of r_{12}; this contribution is large even when the combination of terms 5, 8, and 11 have also been included, though it is somewhat larger when these have not been included. Since the combination of terms 5, 8, and 11 involves radial as well as angular correlation, it is of interest to consider the individual term 11 (involving r^2_{12}) which is essential to the $2p^2$ dependence. Term 11 makes a substantial contribution in the absence of term 2, but this drops to a very small value when term 2 is included. In the inner shell, the r_{12} correlation seems much more important than the $2p^2$ contribution; radial correlation is also rather important.

We have considered the possibility that there may be significant contributions from expansion terms which account for simultaneous correlation in each of the two shells, though this would not be consistent with the notion that over-all correlation energy is very closely approximated by a sum of pair correlation energies. This possibility led us to include the last five terms in Table I. Their over-all contribution is about 0.002 as compared to a remaining error of about 0.006. In order to fully test this possibility it would be necessary to include a term containing both r_{12} and r^2_{34}, since the separate contributions of terms containing each of these factors are quite large. Inclusion of such a term requires relaxation of the restriction mentioned above and the consequent substantial extension of the computer program. A very preliminary result, obtained with an incompletely checked extension of the computer program, suggests that addition of this one expansion term may reduce the remaining error by about one-half. The extended program is, of course, no more general than the combined CI and r_{ij} approach of Sims and Hagstrom,[10] who have already obtained excellent results for Be. (It would seem of interest to apply either the SH method or the essentially equivalent extended Hylleraas method to other four-electron systems, especially Li^-.)

Since SH have arranged their expansion terms so that p orbitals enter only after 92 terms have been included, their results give an excellent indication of the maximum further improvement which could be obtained by the limited Hylleraas approach used herein (with at most one r_{ij}-type factor per expansion term). With 92 terms, SH achieve an energy of −14.6636; this is 0.0025 better than the present 18-term result and about 0.0030 poorer than their final result including p orbitals. Their work shows that inclusion of expansion terms accounting for simultaneous correlation in each of the two shells is indeed important.

TABLE II. Comparison of results of various upper-energy-bound calculations. The Hartree-Fock method is denoted by HF, configuration-interaction methods are denoted by CI, while r^p_{ij} indicates methods employing correlation factors of that functional form (i.e., Hylleraas-type methods).

Reference	Method	Number of terms	$-E$ (a.u.)
Roothaan *et al.*[15]	HF	1	14.5730
Szasz and Byrne[6]	r^p_{ij}	26	14.6565
Watson[17]	CI	37	14.6574
Gentner and Burke[7]	r^p_{ij}	25	14.6579
Weiss[8]	CI	55	14.6609
Present work	r^p_{ij}	18	14.6611
Bunge[9]	CI	180	14.6642
Sims and Hagstrom[10]	r^p_{ij}+CI	107	14.6665
Exact			14.667

In Table II is given a comparison of results of several calculations of the Be ground state by variational methods, which lead to upper-energy-bound estimates. The present 18-term result is slightly better than the 25-term Hylleraas-type result of Gentner and Burke[7] and is very close to the 55-term CI result of Weiss.[8] Considerably better results have been obtained with longer expansions by Bunge[9] and by Sims and Hagstrom.[10] The latter authors combined the Hylleraas and CI approaches, which seems a very favorable combination for the particular state in view of the importance of r_{12} in the inner shell and of a $2p^2$ configuration in the outer shell.

Though limited in scope, the present results do seem to compare favorably with other published results when attention is restricted to moderately short expansions. Results given in the present Table I are somewhat better at each order than results given in Table I of Gentner and Burke,[7] reflecting a difference in the choice of expansion terms. The present results are also better than those given in Table III of SH; this is doubtless mainly a result of the fact that SH did not arrange their expansion terms in order of decreasing energy contribution. The present value of −14.6552 for an 11-term expansion may be compared with the value of −14.6445 for an 11-term expansion as given in Table I of SH and with a value of −14.6529 for a 12-term expansion obtained by adding a $1s^2\,2p^2$ configuration as given in Table II of SH. Thus the SH 12-term result is 0.0023 poorer than the present 11-term result; addition of a further 80 terms improves the SH result by 0.0107, whereas addition of seven terms improves the present result by only 0.0059. Thus the SH 92-term result is better than the comparable present 18-term result by 0.0025. Inclusion of 15 further terms which account for simultaneous correlation in each of the shells gives SH a further improvement of 0.0030 and leads to a result extremely close to the exact value.

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Optical-Pumping Charge-Exchange Method for Studying Nuclear-Spin Orientation in $^1S_0$ Atomic Ions*

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A detailed description is presented of an optical-pumping charge-exchange method for establishing and observing nuclear-spin orientation in atomic ions having a $^1S_0$ electronic configuration. Rb^+, Cs^+, K^+, and free protons have been studied thus far. Various applications of the method include precision measurements of the nuclear moments in the ions and the first measurements of resonant charge-exchange cross sections at thermal energies.

I. INTRODUCTION

In the past, exchange collisions have provided an important mechanism for extending the scope of optical-pumping studies[1] to certain atomic systems that cannot be optically oriented directly. Electron-spin exchange,[2] metastability exchange,[3] and Penning ionization[4] are examples of processes that have been used to transfer spin orientation between optically pumped atoms and other atomic systems of interest. More recently[5,6] we reported on initial successes with another collisional exchange process, resonant charge exchange, which can be used to study singly charged ions and neutral atoms having a $^1S_0$ ground-state electronic configuration. In this paper we will describe in more detail how we have developed this optical-pumping charge-exchange method to make the first studies of nuclear-spin orientation in $^1S_0$ ions. In a subsequent paper we will discuss the application to studying $^1S_0$ atoms.

For measuring nuclear moments, this method with $^1S_0$ ions has the advantage that there is no electronic magnetic moment to complicate the interaction of the system with an external magnetic field. Corresponding measurements of nuclear moments of group IA and IB elements in the parent atoms require separating out the much larger contribution of the electronic magnetic moment. As a result only a few nuclear moments have been measured in such atoms to the few-ppm level.[7,8]

Because the method discussed in this paper is based upon resonant charge exchange, it offers a tool for studying charge-exchange collisions for the first time at thermal energies. Whereas such collisions have been studied extensively at higher energies, there is practically no experimental information in the energy range below 10 eV. In this paper we discuss the determination of cross sections for charge exchange between alkali atoms and ions from linewidths of alkali-