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Combined Configuration-Interaction–Hylleraas-Type Wave-Function Study of the Ground State of the Beryllium Atom*

James S. Sims† and Stanley Hagstrom
Chemistry Department, Indiana University, Bloomington, Indiana 47401

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A method is proposed for the accurate determination of atomic wave functions and energies by the explicit introduction of interelectronic coordinates into a configuration-interaction wave function. This is accomplished by choosing the configurations in the wave function to be antisymmetrized projected products of one-electron functions with powers of interelectronic coordinates. A 107-configuration wave function for the ground state of the beryllium atom was constructed from a basis set consisting of s and p Slater-type orbitals and powers of interelectronic coordinates: r_{ij}^{v} ($v=0, 1, 2$). The energy obtained from this wave function ($E=-14.66654$ a.u.) is an upper bound to the "exact" nonrelativistic energy of this state and it is believed to be within 0.0002 a.u. of the "exact" value. The advantages that the present method offers for extending accurate Hylleraas-method calculations to atomic systems with $N>3$ are discussed.

I. INTRODUCTION

The quantum-mechanical description of atoms and molecules involves the solution of the time-independent Schrödinger equation

$$\mathcal{H}\Psi = E\Psi \tag{1}$$

for the wave function $\Psi = \Psi(X_1, X_2, X_3, \ldots, X_N)$, where $X_i = (\vec{r}_i, \xi_i)$ is the combined space-spin coordinate for electron i. In the case of light atoms, where magnetic interactions can be neglected, $\mathcal{H}$ is the nonrelativistic many-electron Hamiltonian, which in atomic units[1] is

$$\mathcal{H} = \sum_{i=1}^{N}\left(-\tfrac{1}{2}\Delta_i - \frac{\Xi}{r_i}\right) + \sum_{i<j}\frac{1}{r_{ij}} \quad , \tag{2}$$

where Ξ is the nuclear charge and $-\frac{1}{2}\Delta_i$ is the operator corresponding to the kinetic energy of electron i.

One solution to Eq. (1) is that obtained by the Hartree-Fock (HF) method, which has proven useful for evaluating electronic properties described by many one-particle operators (e.g., static electric moments and electric or magnetic polarizabilities).[2] For closed-shell systems, the conventional (or restricted) HF solution to Eq. (1) is a single energy-optimized Slater determinant made up of symmetry-adapted spin orbitals (one-electron functions which are the products of spatial and spin functions). For most open-shell cases, more than one determinant is necessary to ensure that the wave function is an eigenfunction of L^2 and S^2 (again in the conventional or restricted HF method).[3]

Although the conventional HF approximation yields[4] over 99% of the total electronic energies of first-row atoms, it nevertheless fails to be accurate enough for the prediction of two- (or N-) electron properties. Thus, for example, the conventional HF method fails to predict the low-energy cross sections of electron-atom scattering.[5] The accurate computation of quantities like transition probabilities,[6] electron affinities of atoms and ions,[7,8] hyperfine-structure constants,[9] and photoionization cross sections for atoms,[10] atomic ions,[11] and molecules[12] requires solutions of Eq. (1) more accurate than the HF solution.

The two standard variational[13] methods for improving the HF solution were first introduced by Hylleraas[14,15] in a series of papers on heliumlike systems. They are (i) the configuration-interaction (CI) method,[14,16] in which the wave function Ψ is expanded in terms of antisymmetrized and projected products of spin orbitals,[17] and (ii) the Hylleraas (Hy) method,[15,18] in which the interelectronic coordinates r_{ij} are explicitly included in the terms of the wave function. There are theoretical grounds[17,18] for thinking that both the CI and the Hy methods are general methods capable of yielding variational solutions which converge to the exact solution of Eq. (1) with any desired degree of accuracy if a sufficient number of terms are included.

On the basis of calculations on atomic systems with atomic number $N=2$ [19–21] and $N=3$, [20,22] it has generally been held[18,23] that for any N, CI expansions converge much more slowly than Hy-method expansions. On the other hand, (i) the computational difficulties associated with extending the Hy procedure to atomic systems with $N>3$ have been considered so formidable that few calculations of this type have been attempted; (ii) it has been argued[24] that the success of the Hy method for $N=2$ and $N=3$ cannot be extrapolated to heavier atoms; and (iii) recently A. V. Bunge,[25] C. F. Bunge[26] and co-workers,[27] and Schaefer and Harris[8,28] have developed methods for refining the CI method to such a degree that there appears to be no more real theoretical or practical difficulties involved in doing CI calculations.[25]

In view of the above, it seems desirable to examine whether indeed the success of the Hy method can be extrapolated to atomic systems with $N > 3$.[29] To accomplish this, an attempt has been made to formulate a method of explicitly introducing interelectronic coordinates r_{ij} into the wave function, which will be computationally practical for atomic calculations with $N > 3$. This has been done by a method which introduces r_{ij} coordinates into the CI method; i.e., the configurations in the wave function Ψ are chosen to be antisymmetrized projected products of s or p Slater-type orbitals (STO's)[30] with powers of the interelectronic coordinates r_{ij}. This form of the wave function has the following advantages over the expansions in interparticle coordinates[31,32] which characterize all the Hy-method calculations for atoms with $N > 3$ to date[22,33–35]: (i) Products of one-electron functions and at most one r_{ij} power can be used to represent computationally difficult terms of the standard Hy-type wave functions such as "unlinked" products (e.g., $r_{12}r_{34}^2$) in beryllium. (ii) Use of p STO's simplifies the problem of handling nonzero angular momentum states, which arises when one chooses a standard Hy-type wave function. (iii) Important configurations from a CI calclulation in an sp STO basis can be used directly in the wave function, with obvious computational advantages.[36]

The calculations have been done on the beryllium atom because previous applications of the Hy method to beryllium[33–35] have not exposed the success of the Hy method for $N > 3$, and a very refined CI calculation[26] exists for comparison. Also, the mathematical difficulties involved in introducing r_{ij}-dependent terms into wave functions for atoms with an arbitrary number of electrons occur in the beryllium atom. Thus this calculation is a test of the general applicability (for nonrelativistic atomic calculations) of the computational and theoretical techniques developed.

II. WAVE FUNCTION

The variational solution to Eq. (1) that we are seeking is of the form

$$\Psi_{\mathrm{Be}}(X_1, X_2, X_3, X_4) = \textstyle\sum_K C_K \Phi_K (X_1, X_2, X_3, X_4) , \tag{3}$$

where

$$\Phi_K = O(L^2)\, O_{\mathrm{as}} \left(\chi_K r_{ij}^{v_K} \prod_{s=1}^{4} \varphi_{Ks}(\vec{\mathrm{r}}_s) \right) . \tag{4}$$

In Eq. (4), $O(L^2)$ is an idempotent orbital angular momentum projection operator[37] and O_{as} is the projection operator which guarantees the antisymmetry of the wave function

$$O_{\mathrm{as}} = (4!)^{-1} \textstyle\sum_p (-1)^p P , \tag{5}$$

where the summation runs over all the 4! permutations P, with p being the parity of the corresponding permutation P. Also, χ_K is one of the two linearly independent spin functions $\chi_1 = \frac{1}{2}(\alpha_1\beta_2 - \beta_1\alpha_2) \times (\alpha_3\beta_4 - \beta_3\alpha_4)$ and $\chi_2 = \frac{1}{2}(\alpha_1\beta_4 - \beta_1\alpha_4)(\alpha_2\beta_3 - \beta_2\alpha_3)$ which span the four-electron spin space with $S = S_z = 0$. In Eq. (4), $\varphi_{Ks}(\vec{\mathrm{r}}_s)$ refers to the sth basis orbital in the Kth configuration. The orbital basis consists of STO's of the general form

$$\varphi(\vec{\mathrm{r}}) = \frac{(2\zeta)^{n+1/2}}{[(2n)!]^{1/2}} r^{n-1} e^{-\xi r} Y_{l,m} , \tag{6}$$

where the set $\{Y_{l,m}\}$ consists of normalized spherical harmonics in the Dirac phase convention.[38]

The approach that we have followed in seeking a variational solution to Eq. (1) of the form given by Eq. (3) differs from attempts by other authors to use a correlation factor[15,32,39,40] or to combine a correlation factor with the more systematic approach of the CI method.[17,41] The approach that we have followed may be characterized as one which allows for the utilization of a pair correlation factor r_{ij} in those configurations which make the greatest contribution in a CI expansion, in contrast with the attempts to use an average factor for the whole atom (correlation factor).

In Eq. (4) the restriction of only one r_{ij} coordinate per term, which was first proposed by James and Coolidge,[42] has been retained. A standard Hy-type expansion in interparticle coordinates for $N > 3$ gives rise to two different types of products of interelectronic coordinates: (i) the "linked" type, in which at least one electron subscript appears in two or more r_{ij}'s and (ii) the "unlinked" type, in which there are no repeated subscripts. Linked products (e.g., $r_{12}r_{23}$) do not appear very important energetically; evidence of this is the extremely accurate lithium calculation of Larsson[22] in which the one term with more than one r_{ij} coordinate lowered the energy by only 7×10^{-6} a.u. It is felt that important unlinked products of r_{ij} coordinates can be represented within an sp STO, r_{ij}^v basis by a single r_{ij}^v factor and excited orbitals from the STO basis.[43] For these reasons, the limitation of only one r_{ij} coordinate per term is not felt to be a severe limitation for the wave function of Eq. (4).

There is some indication of how well one might expect to do with the restricted basis: The sp STO basis r_{ij}^v $(v = 0, 1, 2)$ has recently been given by Bunge.[44] In his paper on the He atom, Bunge examines the six-term wave function of Hylleraas[15(a)] $(\Psi_{6\mathrm{Hy}})$ in terms of angular energy limits. He finds that the sp-limit energy error of $\Psi_{6\mathrm{Hy}}$ (when compared with his estimate of the "exact" sp limit) is identical to the total energy error of $\Psi_{6\mathrm{Hy}}$ to six decimal places (a.u.). He then concludes that one should be able to compute helium wave functions with energy errors smaller than 10^{-6} a.u. by taking the direct product of a suitable sp basis and the $\Psi_{6\mathrm{Hy}}$ (an s basis and r_{12}^{v}, $v=0,1,2$). While there are still questions concerning the validity of extrapolating the successes of calculations on helium to other atomic systems,[29] this analysis clearly indicates that such a restricted basis might be an excellent one for states of first-row atoms.

III. METHOD OF CALCULATION

A. $O(L^2)$ Projection

Since $O(L^2)$ is a product of terms involving the operator L^2,[37] the commutation of $O(L^2)$ and $r_{ij}^{v_K}$ follows from the commutation of L^2 and $r_{ij}^{v_K}$. Since $O(L^2)$ and O_{as} commute, the $O(L^2)$ projection in Eq. (4) reduces to a projection on the four-orbital Hartree product

$$\prod_{s=1}^{4} \varphi_{Ks}(\vec{r}_s).$$

The results of this projection have been tabulated by Bunge[45]; the Bunge explicit formulas were used in this calculation.[46]

B. Choice of Spin Function

The linearly independent spin functions chosen in this work are the valence bond (VB) spin functions,[47] corresponding to $S=S_z=0$:

$$\begin{aligned}\chi_1 &= \tfrac{1}{2}(\alpha_1\beta_2-\beta_1\alpha_2)(\alpha_3\beta_4-\beta_3\alpha_4)\ ,\\ \chi_2 &= \tfrac{1}{2}(\alpha_1\beta_4-\beta_1\alpha_4)(\alpha_2\beta_3-\beta_2\alpha_3)\ .\end{aligned} \tag{7}$$

The two VB functions are related by a permutation; specifically,

$$P_{13}=\begin{pmatrix}1234\\3214\end{pmatrix}$$

has the effect of taking χ_2 into χ_1:

$$\begin{aligned}P_{13}\chi_2 &= \frac{1}{2}\begin{pmatrix}1234\\3214\end{pmatrix}\\ &\quad\times(\alpha_1\alpha_2\beta_3\beta_4-\alpha_1\beta_2\alpha_3\beta_4-\beta_1\alpha_2\beta_3\alpha_4+\beta_1\beta_2\alpha_3\alpha_4)\\ &= -\tfrac{1}{2}(\alpha_1\beta_2\alpha_3\beta_4-\alpha_1\beta_2\beta_3\alpha_4-\beta_1\alpha_2\alpha_3\beta_4+\beta_1\alpha_2\beta_3\alpha_4)\\ &= -\chi_1\ .\end{aligned} \tag{8}$$

It should be noted that a term (configuration) formed from the second spin function χ_2 and a particular choice of r_{ij} factor and Hartree product,

$$F_K(\vec{r}_1,\ \vec{r}_2,\ \vec{r}_3,\ \vec{r}_4)=r_{ij}^{v_K}\prod_{s=1}^{4}\varphi_{Ks}(\vec{r}_s)\ , \tag{9}$$

is equivalent to the term formed from the first spin function χ_1 and the choice of r_{ij} factor and Hartree product $P_{13}F_K$. This can be seen from the relationships

$$|\Phi_K| = |O(L^2)O_{\mathrm{as}}\{\chi_2F_K\}| = |O(L^2)O_{\mathrm{as}}\{\chi_1P_{13}F_K\}|\ , \tag{10}$$

which follow from Eq. (8) and an identity for the antisymmetrizer $O_{\mathrm{as}}=(-1)^{p}P^{r}P^{\sigma}$ (P^{r} permutes only the space coordinates and P^{σ} permutes only the spin coordinates). Thus it is possible to converge upon the exact wave function by employing only one spin function.

In practice one usually chooses F_K such that the energy lowering is appreciable and such that the correct localization of the electron orbitals is given (through the values of inner- and outer-shell orbital exponents). The configuration formed from F_K and χ_2, or, equivalently, the configuration formed from $P_{13}F_K$ and χ_1, would not be expected to give a good energy lowering. Thus, when a few configurations containing the second spin function were tried, their effect was negligible (to 10^{-6} a.u.). These observations and results parallel those of Larsson[22] for the ^2S ground state of lithium, although he found that the second spin function made important adjustments to the Fermi contact term. Since the emphasis here is on obtaining a good energy, the final 107-configuration wave function resulted from only terms with the spin function χ_1.

The method used to generate VB spin functions and to evaluate matrix elements over VB spin functions was developed by E. A. Scarzafava.[48] The explicit formula for the Hamiltonian matrix element after integration over spin coordinates is ($\chi_K=\chi_L=\chi_1$),[46]

$$\begin{aligned}H_{KL} &= \langle\Phi_K|\mathcal{H}|\Phi_L\rangle\\ &= (1/4!)\langle O(L^2)A^{\alpha}A^{\beta}S_1^{r}F_K|\mathcal{H}|S_1^{r}F_L\rangle\ ,\end{aligned} \tag{11}$$

where $A^{\alpha}A^{\beta}=(1-P_{13}^{r})(1-P_{24}^{r})$ is a product of space-pair antisymmetrizers (un-normalized), and $S_1^{r}=\tfrac{1}{2}(1+P_{12}^{r})(1+P_{34}^{r})$ is a product of commuting space-pair symmetrizers (normalized).

C. Integral Treatment

To complete the evaluation of the Hamiltonian matrix element H_{KL}, a scheme is needed to handle the two-, three-, and four-electron integrals of the form

$$\int f_1(\vec{r}_1)f_2(\vec{r}_2)f_3(\vec{r}_3)f_4(\vec{r}_4)\,g_1(r_{12})\times g_2(r_{23})\cdots g_k(r_{34})\,dv. \tag{12}$$

A good scheme for the evaluation of three-electron integrals of this form containing nonspherically symmetrical STO's has been formulated by Öhrn and Nordling.[49] Their scheme has been extended in this work to the treatment of four-electron integrals. Also, the Öhrn and Nordling scheme for the evaluation of their V and W auxiliary integrals involves

TABLE I. 11-configuration wave function for the ground state of atomic beryllium with the energy for various basis-set orbital exponents.

Wave function (Φ_{11}) Configuration No.		Energy for various basis-set orbital exponents ζs		
	Configuration[a]	ζs	$\zeta s''$	Energy (a. u.)
1	$1s^2 3s'' 2s''$			
2	$1s^2 4s'' 2s''$			
3	$1s^2 5s'' 2s''$			
4	$1s^2 6s'' 2s''$	3.6847	0.9562	−14.644518
5	$2s 1s 2s''^2$	3.6848	0.9560	−14.644507
6	$3s 1s 2s''^2$	3.7	0.9	−14.644077
7	$4s 1s 2s''^2$			
8	$1s^2 2s''^2$			
9	$1s^2 2s''^2 r_{12}$			
10	$1s^2 2s''^2 r_{12}^2$			
11	$1s^2 2s''^2 r_{34}$			

[a]For a definition of the notation used, see Sec. IV.

infinite summations; in this work, McKoy's[50] closed-form formulas for certain of these auxiliary integrals were used. In some instances McKoy's formulas were found to lead to significant differencing errors; a stable computational procedure was found for this region by using Euler's method[51] to transform McKoy's formulas.[52] We intend to describe our integral treatment in more detail in another paper.[52]

IV. CHOICE OF PARAMETERS AND CONFIGURATIONS

The wave function employed here for the ^1S ground state of beryllium is of the form [Eq. (3)]

$$\Psi_I = \sum_K C_K^I \Phi_K , \tag{13}$$

where Φ_K is a properly antisymmetrized and projected product of χ_1, STO's defined by Eq. (6), and an $r_{ij}^{v_K}$ factor. By minimizing the energy with respect to the coefficients C_K^I, one is led to the usual secular equation with the Ith lowest root being an upper bound to the exact energy of the respective state. The secular equation is solved by Jacobi's method[53] after the overlap matrix has been triangulated and the Hamiltonian matrix transformed by the method of Michels, Van Dine, and Elliott.[54]

In order to determine the orbital exponents of the STO basis, three 11-configuration calculations were performed. The wave function is given in Table I, where under configuration is listed only the unique

$$r_{ij}^{v_K} \prod_{s=1}^{4} \varphi_{Ks}(\vec{r}_s)$$

part of Φ_K ($\chi_K = \chi_1$) as defined by Eq. (4). The STO basis is, in the Weiss notation,[55] the basis set $1s$, $2s$, ..., ns; $1s''$, ..., ns''. The first basis-set orbital exponents $\zeta_s = 3.6847$, $\zeta_{s''} = 0.9562$,[56,57] were chosen to repeat the 11-configuration calculation of Karl.[35] Next two other sets of orbital exponents were tried: the set $\zeta_s = 3.6848$, $\zeta_{s''} = 0.9560$[58] and the set $\zeta_s = 3.7$, $\zeta_{s''} = 0.9$. Neither case did as well as the first set (see Table I). Therefore, $\zeta_s = 3.6847$ and $\zeta_{s''} = 0.9562$ were chosen for the remaining calculations.

The effect of not having done an exhaustive minimization at this point is not felt to be significant because other investigators have found that the orbital exponents have very little dependence on the presence or absence of an r_{ij} coordinate.[22,23] In addition, configurations containing inner-shell ns' orbitals ($\zeta_{s'} = 7.8$) and some of the "open-shell" configurations of Gentner and Burke[34] ($\zeta_{s'''} = 2.3$ in outer-shell orbitals) were added to larger calculations and found to give insignificant energy improvements.

Next, the various 12-configuration calculations displayed in Table II were performed in order to (i) determine $\zeta_{p''}$ and (ii) test how well the r_{34}^2 terms can represent the well-known $2s$-$2p$ near degeneracy in beryllium. Since the Weiss $\zeta_{p''} = 1.1$ proved superior to $\zeta_{p''} = 0.9562$, in the remaining calculations $\zeta_{p''} = 1.1$ was used and the Weiss value $\zeta_p = 6.2$ was used for the K shell. Also it should be noted that neither $1s^2 2s''^2 r_{34}^2$ nor $1s^2 1s''^2 r_{34}^2$ does nearly as well as $1s^2 2p''^2$.

Next, configurations related to the best of the 12-configuration wave function and also some new configurations were added to the 12-configuration wave function; those which gave only a small energy improvement were dropped. The process was continued until almost all conceivable combinations were tried, resulting in a final 107-configuration wave function. The terms in the best 107-configuration wave function were grouped by type and by the magnitude of their coefficients; configurations were then successively removed one by one until the $1s^2 2s''^2$ configuration was reached.

V. RESULTS

The final 107-configuration wave function is displayed in Table III, along with the energy $E(n)$ for the n-configuration wave function (configurations 1–n) and the estimate of the energy contribution of each configuration obtained from $E(n) - E(n-1)$.

The 1-configuration wave function is an approximation to the HF function and the energy of the 1-configuration wave function, $E = -14.55674$ a.u., is close to the HF energy of -14.57302 a.u.[58] The 22-configuration energy of -14.588316 a.u. is not

TABLE II. 12-configuration wave functions and energies for the ground state of atomic beryllium.

Energy (a. u.)	$\zeta_{p''}$	Wave function
−14.6465	...	$\Phi_{11} + 1s^2 2s''^2 r_{34}^2$ [a]
−14.6480	...	$\Phi_{11} + 1s^2 1s''^2 r_{34}^2$
−14.6514	0.9562	$\Phi_{11} + 1s^2 2p''^2$
−14.6529	1.1	$\Phi_{11} + 1s^2 2p''^2$

[a]From Table I; $\zeta_s = 3.6847$, $\zeta_{s''} = 0.9562$.

TABLE III. 107-configuration wave function for the ^1S ground state of atomic beryllium, with the energy contribution of each configuration.

Configuration No. n	Configuration[a]	Energy $E(n)$ of n-configuration function (a.u.)	Energy contribution $E(n)-E(n-1)$, (a.u.)	Coefficient 107-term (unnormalized) wave function
1	$1s^2\,2s''^2$	−14.556 739 82	• • •	1.375 968 83
2	$1s^2\,3s'''\,2s''$	−14.556 739 86	−0.000 000 04	$5.910\,075\,488\times10^{-1}$
3	$1s^2\,4s''\,2s''$	−14.556 857 85	−0.000 117 99	$-1.413\,423\,429\times10^{1}$
4	$1s^2\,5s''\,2s''$	−14.558 370 51	−0.001 512 66	$4.505\,907\,738\times10^{1}$
5	$1s^2\,6s''\,2s'''$	−14.559 457 17	−0.001 086 66	$-6.411\,900\,926\times10^{1}$
6	$1s^2\,7s''\,2s''$	−14.559 990 03	−0.000 532 86	$3.443\,485\,406\times10^{1}$
7	$1s^2\,8s''\,2s''$	−14.560 174 84	−0.000 184 81	$-6.168\,935\,363\times10^{-2}$
8	$2s1s\,2s''^2$	−14.560 224 57	−0.000 049 73	$-9.515\,335\,546\times10^{-2}$
9	$3s1s\,2s''^2$	−14.571 713 70	−0.011 489 13	$1.670\,736\,912\times10^{-1}$
10	$2s1s\,3s''\,2s''$	−14.571 848 14	−0.000 134 44	−1.117 889 188
11	$2s1s\,4s''\,2s''$	−14.572 010 75	−0.000 162 61	$5.929\,294\,805\times10^{-1}$
12	$2s1s\,5s''\,2s''$	−14.572 185 32	−0.000 174 51	$-1.691\,288\,463\times10^{-1}$
13	$2s1s\,6s''\,2s''$	−14.572 356 78	−0.000 171 46	$1.880\,474\,865\times10^{-2}$
14	$1s^2\,4s''\,3s'''$	−14.574 959 44	−0.002 602 66	$7.413\,007\,028\times10^{-1}$
15	$1s^2\,5s''\,3s'''$	−14.575 399 88	−0.000 440 44	$-2.196\,819\,680\times10^{-1}$
16	$1s^2\,1s''\,2s''$	−14.575 536 30	−0.000 136 42	$-2.106\,580\,433\times10^{-1}$
17	$1s^2\,3s''^2$	−14.575 536 96	−0.000 000 66	$1.494\,281\,330\times10^{-2}$
18	$1s^2\,4s''^2$	−14.575 616 62	−0.000 079 66	$-1.495\,501\,172\times10^{-1}$
19	$1s^2\,2s''^2$	−14.588 132 27	−0.012 515 65	$-4.668\,310\,312\times10^{-1}$
20	$2s^2\,3s''^2$	−14.588 169 33	−0.000 037 06	$2.405\,264\,606\,9\times10^{-2}$
21	$3s1s\,3s''^2$	−14.588 295 77	−0.000 126 44	$-2.089\,966\,004\times10^{-2}$
22	$2s^2\,1s''^2$	−14.588 316 53	−0.000 020 76	$-8.506\,222\,906\times10^{-3}$
23	$1s^2\,2s''^2\,r_{34}^2$	−14.607 556 94	−0.019 240 41	1.242 582 659
24	$1s^2\,2s''^2\,r_{34}$	−14.620 767 20	−0.013 210 26	$7.353\,963\,998\times10^{-1}$
25	$1s^2\,2s'''^2\,r_{12}$	−14.647 872 00	−0.027 104 80	$3.113\,830\,843\times10^{-1}$
26	$1s^2\,2s'''^2\,r_{12}^2$	−14.650 381 51	−0.002 509 51	$-1.424\,319\,613\times10^{-1}$
27	$1s^2\,3s''\,2s''\,r_{34}$	−14.653 676 28	−0.003 294 77	$3.623\,219\,838\times10^{-1}$
28	$1s^2\,4s''\,2s''\,r_{34}$	−14.654 554 23	−0.000 877 95	−1.265 531 509
29	$1s^2\,5s''\,2s''\,r_{34}$	−14.654 993 26	−0.000 439 03	$5.890\,023\,621\times10^{-1}$
30	$1s^2\,3s''\,2s''\,r_{34}^2$	−14.655 060 61	−0.000 067 35	$-2.240\,200\,835\times10^{-1}$
31	$1s^2\,4s''\,2s''\,r_{34}^2$	−14.655 167 08	−0.000 106 47	$-1.970\,202\,929\times10^{-1}$
32	$1s^2\,3s''\,2s''\,r_{12}^2$	−14.655 172 84	−0.000 005 76	$-1.169\,538\,943\times10^{-1}$
33	$1s^2\,4s''\,2s''\,r_{12}^2$	−14.655 207 15	−0.000 034 31	$5.214\,784\,011\times10^{-2}$
34	$1s^2\,5s''\,2s''\,r_{12}^2$	−14.655 317 46	−0.000 110 31	$-8.219\,871\,428\times10^{-3}$
35	$2s1s\,2s''^2\,r_{12}^2$	−14.655 417 64	−0.000 100 18	$1.443\,626\,383\times10^{-1}$
36	$3s1s\,2s''^2\,r_{12}^2$	−14.655 546 67	−0.000 129 03	$7.648\,054\,921\times10^{-3}$
37	$4s1s\,2s''^2\,r_{12}^2$	−14.655 630 55	−0.000 083 88	$-2.470\,285\,589\times10^{-3}$
38	$2s1s\,2s''^2\,r_{12}$	−14.655 790 79	−0.000 160 24	$4.436\,421\,887\times10^{-2}$
39	$3s1s\,2s''^2\,r_{12}$	−14.655 830 54	−0.000 039 75	$-1.291\,085\,746\times10^{-1}$
40	$4s1s\,2s''^2\,r_{12}$	−14.655 859 40	−0.000 028 86	$1.261\,377\,873\times10^{-2}$
41	$2s^2\,2s''^2\,r_{12}$	−14.655 861 93	−0.000 002 53	$2.654\,673\,541\times10^{-2}$
43	$2s^2\,2s''^2\,r_{12}^2$	−14.655 939 30	−0.000 077 37	$-2.026\,828\,034\times10^{-2}$
43	$2s^2\,2s''^2\,r_{34}$	−14.656 111 19	−0.000 171 89	$-5.773\,520\,713\times10^{-2}$
44	$2s^2\,2s''^2\,r_{34}^2$	−14.656 122 75	−0.000 011 56	$5.823\,923\,946\times10^{-3}$
45	$1s^2\,3s''^2\,r_{12}$	−14.656 178 44	−0.000 055 79	$-3.657\,164\,415\times10^{-2}$
46	$1s^2\,3s'''^2\,r_{12}^2$	−14.656 180 07	−0.000 001 63	$3.751\,225\,625\times10^{-2}$
47	$1s^2\,1s''^2\,r_{12}$	−14.656 399 18	−0.000 219 11	$-1.359\,655\,042\times10^{-2}$
48	$1s^2\,1s''^2\,r_{34}$	−14.657 329 58	−0.000 930 40	$-7.555\,111\,368\times10^{-2}$
49	$1s^2\,1s''^2\,r_{34}^2$	−14.658 512 81	−0.001 183 23	$-2.362\,562\,296\times10^{-2}$
50	$2s1s\,3s''^2\,r_{12}^2$	−14.658 727 68	−0.000 214 87	$1.862\,067\,443\times10^{-4}$
51	$1s^2\,4s''^2\,r_{34}$	−14.658 730 29	−0.000 002 61	$6.550\,189\,840\times10^{-2}$
52	$1s^2\,4s''^2\,r_{12}^2$	−14.658 769 72	−0.000 039 43	$-5.084\,412\,549\times10^{-3}$
53	$2s1s\,2s''^2\,r_{34}$	−14.659 282 83	−0.000 513 11	$3.532\,770\,113\times10^{-2}$
54	$3s1s\,2s''^2\,r_{34}$	−14.659 991 56	−0.000 708 73	$3.672\,615\,695\times10^{-2}$
55	$2s^2\,3s''^2\,r_{12}$	−14.659 992 27	−0.000 000 71	$-8.963\,829\,877\times10^{-3}$
56	$2s^2\,3s''^2\,r_{34}$	−14.660 003 54	−0.000 011 27	$3.068\,319\,941\times10^{-3}$

TABLE III. (*Continued*)

Configuration No. n	Configuration[a]	Energy $E(n)$ of n-configuration function (a.u.)	Energy contribution $E(n)-E(n-1)$, (a.u.)	Coefficient 107-term (unnormalized) wave function
57	$2s^2\,1s''^2\,r_{12}^2$	−14.660 033 05	−0.000 029 51	$-6.703\,544\,743\times10^{-3}$
58	$2s1s\;2s''^2\,r_{34}^2$	−14.660 054 60	−0.000 021 55	$-1.300\,546\,033\times10^{-2}$
59	$3s1s\;2s''^2\,r_{34}^2$	−14.660 075 22	−0.000 020 62	$8.192\,479\,333\times10^{-3}$
60	$4s1s\;2s''^2\,r_{34}^2$	−14.660 111 78	−0.000 036 56	$-5.401\,901\,555\times10^{-3}$
61	$1s^2\,3s''^2\,r_{34}^2$	−14.660 111 95	−0.000 000 17	$-7.906\,469\,502\times10^{-3}$
62	$1s^2\,3s''^2\,r_{34}$	−14.660 112 50	−0.000 000 55	$-1.398\,060\,670\times10^{-2}$
63	$1s^2\,2s''^2\,r_{13}$	−14.661 208 65	−0.001 096 15	$-2.429\,212\,061$
64	$1s^2\,1s''2s''\,r_{13}$	−14.662 435 93	−0.001 227 28	$1.010\,637\,493$
65	$1s^2\,3s''2s''\,r_{13}$	−14.662 436 02	−0.000 000 09	$2.333\,595\,641\times10^{1}$
66	$1s^2\,4s''2s''\,r_{13}$	−14.662 452 19	−0.000 016 17	$-8.317\,840\,025\times10^{1}$
67	$1s^2\,5s''2s''\,r_{13}$	−14.662 463 82	−0.000 011 63	$1.226\,970\,702\times10^{2}$
68	$1s^2\,6s''\,2s''\,r_{13}$	−14.662 464 59	−0.000 000 77	$-6.688\,201\,230\times10^{1}$
69	$1s^2\,2s''^2\,r_{13}^2$	−14.662 494 34	−0.000 029 75	$-1.010\,450\,088\times10^{1}$
70	$1s^2\,3s''2s''\,r_{13}^2$	−14.662 508 85	−0.000 014 51	$3.919\,367\,631\times10^{1}$
71	$1s^2\,4s''2s''\,r_{13}^2$	−14.662 529 67	−0.000 020 82	$-5.921\,306\,844\times10^{1}$
72	$1s^2\,5s''2s''\,r_{13}^2$	−14.662 590 20	−0.000 060 53	$3.269\,302\,918\times10^{1}$
73	$1s^2\,3s''2s''\,r_{24}^2$	−14.662 648 72	−0.000 058 52	$7.076\,308\,541\times10^{-1}$
74	$1s^2\,4s''2s''\,r_{24}^2$	−14.662 691 66	−0.000 042 94	$-7.641\,050\,527\times10^{-2}$
75	$1s^2\,5s''2s''\,r_{24}^2$	−14.662 707 98	−0.000 016 32	$-7.032\,753\,091\times10^{-2}$
76	$2s1s\;2s''^2\,r_{13}^2$	−14.662 768 58	−0.000 060 60	$-2.701\,382\,819\times10^{-1}$
77	$3s1s\;2s''^2\,r_{13}^2$	−14.662 800 60	−0.000 032 02	$3.183\,369\,817\times10^{-2}$
78	$1s^2\,3s''^2\,r_{13}^2$	−14.662 816 88	−0.000 016 28	$-2.636\,753\,100\times10^{-1}$
79	$2s1s\;2s''^2\,r_{13}$	−14.663 067 10	−0.000 250 22	$8.671\,072\,552\times10^{-1}$
80	$3s1s\;2s''^2\,r_{13}$	−14.663 067 28	−0.000 000 18	$-1.042\,006\,362\times10^{-1}$
81	$1s^2\,1s''^2\,r_{13}^2$	−14.663 498 43	−0.000 431 15	$2.772\,584\,514\times10^{-2}$
82	$1s^2\,3s''^2\,r_{13}$	−14.663 498 84	−0.000 000 41	$-1.188\,093\,091\times10^{-1}$
83	$1s^2\,4s''^2\,r_{13}$	−14.663 502 13	−0.000 003 29	$1.206\,853\,851\times10^{-1}$
84	$2s^2\,2s''^2\,r_{13}$	−14.663 502 96	−0.000 000 83	$7.058\,385\,812\times10^{-3}$
85	$1s^2\,1s''^2\,r_{13}$	−14.663 513 79	−0.000 010 83	$-2.828\,054\,601\times10^{-1}$
86	$1s^2\,3s''2s''\,r_{24}$	−14.663 516 16	−0.000 002 37	$-8.479\,834\,642\times10^{-1}$
87	$1s^2\,4s''2s''\,r_{24}$	−14.663 537 70	−0.000 021 54	$5.482\,149\,284\times10^{-2}$
88	$1s^2\,5s''2s''\,r_{24}$	−14.663 545 85	−0.000 008 15	$8.709\,265\,657\times10^{-2}$
89	$2s1s\;2s''^2\,r_{24}$	−14.663 566 73	−0.000 020 88	$-1.054\,300\,751\times10^{-1}$
90	$1s^2\,6s''2s''\,r_{24}$	−14.663 567 59	−0.000 000 86	$1.684\,944\,651\times10^{-2}$
91	$2s1s\;2s''^2\,r_{24}$	−14.663 572 62	−0.000 005 03	$4.183\,593\,501\times10^{-2}$
92	$2s1s\;3s''2s''\,r_{24}^2$	−14.663 583 03	−0.000 010 41	$1.314\,304\,853\times10^{-2}$
93	$1s^2\,3p''^2$	−14.663 583 11	−0.000 000 08	$5.218\,659\,990\times10^{-1}$
94	$1s^2\,2p''^2$	−14.663 630 11	−0.000 047 00	$-1.409\,783\,443\times10^{-1}$
95	$1s^2\,3p''2p''$	−14.663 678 88	−0.000 048 77	$-1.954\,639\,743\times10^{-1}$
96	$1s^2\,2p''^2\,r_{12}^2$	−14.664 912 82	−0.001 233 94	$1.815\,973\,512\times10^{-2}$
97	$1s^2\,2p''^2\,r_{12}$	−14.666 097 10	−0.001 184 28	$-6.389\,885\,865\times10^{-2}$
98	$2s1s\;2p''^2$	−14.666 300 86	−0.000 203 76	$6.631\,045\,101\times10^{-2}$
99	$3s1s\;2p''^2$	−14.666 463 91	−0.000 163 05	$-2.992\,109\,286\times10^{-2}$
100	$2p^2\,2s''^2$	−14.666 474 28	−0.000 010 37	$7.725\,719\,831\times10^{-3}$
101	$2p^2\,2s''^2\,r_{12}$	−14.666 513 25	−0.000 038 97	$-7.914\,756\,166\times10^{-3}$
102	$1s\;2p2p''\;2s''$	−14.666 513 84	−0.000 000 59	$-1.033\,981\,466\times10^{-2}$
103	$1s\;3p3p''\;2s''$	−14.666 514 72	−0.000 000 88	$-7.282\,806\,240\times10^{-3}$
104	$1s\;2p^2\,2s''$	−14.666 539 25	−0.000 024 53	$2.172\,123\,776\times10^{-3}$
105	$1s\;2p''^2\,2s''$	−14.666 544 84	−0.000 005 59	$-1.771\,692\,106\times10^{-3}$
106	$3s1s\;3s''2s''$	−14.666 546 47	−0.000 001 62	$9.255\,210\,743\times10^{-2}$
107	$3s1s\;4s''2s''$	−14.666 546 58	−0.000 000 12	$-3.268\,371\,201\times10^{-2}$

[a] For a definition of the notation used, see Sec. IV.

TABLE IV. Comparison of various *ab initio*[a] variational calculations on the ground state of the beryllium atom.

Reference	Wave function employed	Energy (a.u.)
35	13-term Hy type	−14.6497
Sabelli and Hinze[b]	10-term multiconfiguration self-consistent field	−14.65464
33	27-term Hy type; no intershell terms	−14.6565
59	37-term CI	−14.65740
34	25-term Hy type: includes intershell terms.	−14.6579
20	55-term CI	−14.66090
61	28-term augmented separated pair.	−14.66179
Present work	59-term Hy type.	−14.66325
Present work	92-term Hy type.	−14.66358
26[c]	180-term CI	−14.66419
Present work	107-term combined CI Hy type.	−14.66654
Upper bound, 26[c]		−14.66639
"Exact," 26[c]		−14.6667
"Exact," 61		−14.66731

[a] By *ab initio* is meant [L. C. Allen and A. M. Karo, Rev. Mod. Phys. 32, 275 (1960)] use of the exact nonrelativistic Hamiltonian, consideration of all electrons simultaneously, and evaluation of all integrals as accurately as necessary.

[b] N. Sabelli and J. Hinze, J. Chem. Phys. 50, 684 (1969).

[c] Thought to be the most reliable estimate (see Sec. V).

as good as the Weiss[20] value of −14.59110 a.u. for his more extensive s-basis set. This is because (i) the Weiss configurations containing s' and s''' orbitals were added to more extensive wave functions containing powers of r_{12} and r_{34}. In these calculations, the effect of configurations containing s' and s''' orbitals was observed to be negligible (to 10^{-6} a.u.). (ii) The 107-configuration wave function can be simplified without appreciably effecting the energy; thus, for example, a 94-configuration truncation of the 107-configuration wave function was found with an energy of $E = -14.666505$ a.u.

The energy results obtained with a 107-term wave function are tabulated in Table IV and compared with a number of *ab initio* variational calculations. Previous Hy-method calculations[33–35] have not been able to match the success of the Weiss[20] 55-configuration calculation, whereas in the present work we have found a 59-term Hy-type wave function with an energy improvement of 0.00235 a.u. over the Weiss wave function. The 92-term wave function contained in the final 107-term wave function is of the type employed in all the previous Hy-method calculations for atoms with $N \geq 3$.[22,33–35] Comparing it with the 59-term wave function indicates that the convergence is slow towards the end of the conventional Hy-type expansion. In contrast, inclusion of the p STO's, which Bunge has shown give an excellent basis (when combined with a conventional Hy basis) for the K shell, and which for small calculations (Table III) are more important than r_{34}^2 terms in the L shell, apparently speeds the convergence.

Inspection of Table III shows that the $2s$-$2p$ degeneracy has been represented to a great degree by terms containing r_{34}^2. Apparently the importance of the p STO basis for this calculation is primarily due to the configurations $1s^2\,2p''^2\,r_{12}$ and $1s^2\,2p''^2\,r_{12}^2$, which are the four-excitations arising from a correlated electron-pair wave function Ω

$$\Omega = O_{as}\,\{K(1,\,2)\;L(3,\,4)\}, \qquad (14)$$

but without the strong orthogonality condition. Their relative importance can be explained by the fact that the $2p''^2$ configuration alone contributes ~90% of the L-shell correlation energy[59,60] and configurations containing r_{12} and r_{12}^2 are very important in the K shell.

The final 107-term wave function obtained after examining approximately 145 terms formed from an $s\,p$ STO, r_{ij}^v ($v = 0, 1, 2$) basis and keeping the most important, yields an energy of −14.66654 a.u. This compares favorably with the Bunge[26] 180-term CI wave function obtained after examining approximately 1000 terms (Table IV).

The "exact" energy for the nonrelativisitic Hamiltonian in Eq. (2) has been estimated by several authors[59,61,62] from experimental data by making corrections for relativistic effects. Only the latest estimate of this type,[61] based upon the nonrelativistic corrections of Hartmann and Clementi[63] computed with a HF wave function, has been included in Table IV.

In contrast, Bunge[26] has estimated the exact energy by studying patterns of convergence based upon his 180-term Be wave function and his work on Be^{++}.[44] Since this is an extrapolation from a highly accurate direct solution of Eq. (1), with an error which is estimated to be not greater than 0.0003 a.u., $E = -14.66639$ a.u. is taken as an upper bound to the exact nonrelativistic energy. Adding to this the error estimate 0.0003 a.u. yields a lower bound of −14.6667 a.u., and our final wave function yields an energy within 0.0002 a.u. (≈ 0.005 eV) of the Bunge exact energy.

In building up the wave function, terms which contributed only slightly were dropped and the energy loss on dropping them was computed. In this way

38 terms were dropped; their inclusion in a 145-term wave function could lower the energy no more than 0.000072 a.u. (the sum of the energy losses on dropping these terms at various stages of the computation). This tends to indicate that our wave function is converging to an exact energy within the limits of the Bunge estimate.

VI. CONCLUSIONS

On the basis of the results presented here, it seems reasonable to conclude that the introduction of r_{ij} coordinates into an atomic wave function with $N > 3$ is computationally practical. The basis consisting of an sp STO basis and r_{ij}^{v} ($v = 0, 1, 2$) is indeed excellent for beryllium, yielding an upper bound to the ground state of greater accuracy than can be practically obtained by CI expansions at present. (Compare the $spdfg$ energy limit of Bunge,[26] $E = -14.66598$ a.u.)

The inclusion of p STO's gives more flexibility to the wave function and leads to simpler expansions for the KL shells. But the real significance of including the p STO's appears to be in dealing with the four-excitations arising from a correlated electron-pair wave function $\{K(1, 2)\,L(3, 4)\}$. Thus it has been found that the terms $1s^2 2p''^2 r_{12}$ and $1s^2 2p''^2 r_{12}^2$ are important four-excitations. In a standard Hy-method calculation the effect of these terms would have to be represented by configurations containing products of r_{ij} coordinates (such as $r_{12} r_{34}^2$ and $r_{12}^2 r_{34}^2$), which have proven computationally difficult to deal with.

In conclusion, the present method appears to offer distinct advantages for extending accurate Hy-method calculations to atomic systems with $N > 3$.

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†National Institute of Health Predoctoral Fellow, 1966–1968. Present address: Mail Stop 245-4 NASA/Ames Research Center, Moffett Field, Calif. 94035.

[1] The atomic unit of energy is chosen as $\mu e^4/\hbar^2 = 1$ a.u. (of energy), where μ is the reduced mass of the electron: $\mu = m_e m_N/(m_e + m_N)$.

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pair of electrons, or that cumbersome products of powers of r_{ij} coordinates will be required.

[30] The STO notation that we use [see Eq. (6) in the text] and some of the STO's themselves are from A. W. Weiss, Ref. 20.

[31] Interparticle coordinates are the magnitudes of the distances between each pair of particles in an atomic or molecular system. For an atom, these are the interelectronic distances r_{ij} and the electron-nuclear distances r_i. See, e.g., Ref. 32.

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