approximations that have been made. The crude value for the quadrupole moment obtainable from the measured B supports the more precise atomic-beam result.

C. Core Polarization

Evidence for the core-polarization magnetic field at the nucleus of $4d$ atoms or ions is much more sparse than for the corresponding $3d$ transition series. For $4d$ ions there exist two relevant measurements on the Mo^{5+} ion[17] and the Pd metal.[18] Both results lend support to the hypothesis of a core-polarization field of roughly $-350\,000$ G per unit spin. As mentioned above, an inspection of Eq. (4) reveals that the core polarization of the d electron in the ${}^3P_1$ level of the Pd atom is very small. The contribution from the $d_{5/2}$ state is equal and opposite to the contribution from the $d_{3/2}$ state and both states enter Eq. (4) in roughly the same amounts. Assuming a field of $-350\,000$ G per unit spin, as suggested above, we find that the net contribution is 10 Mc/sec. This is of the same order as the experimental error. Moreover, relativistic corrections to the hfs interaction constants as well as an admixture of configurations containing unpaired s electrons are also expected to be of this magnitude. Consequently, no conclusion concerning core polarization can be drawn from our experiments.

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[18] J. A. Seitchik, A. C. Gossard, and V. Jaccarino, Phys. Rev. **136**, A1119 (1964).

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Electronic Wave Functions for Atoms. I. Ground State of Be*

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A strategy is proposed to determine atomic wave functions by the configuration-interaction method (CI). A large nonoptimized set of Slater-type orbitals (STO's) is contracted into an orthogonal set of smaller dimension whose elements are natural orbitals (NO's) of a CI wave function which includes the Hartree-Fock (HF) configuration and, out of all possible double excitations, only those such that the HF orbitals are also NO's. Conceptual and practical arguments which justify such a procedure are given. A nonrelativistic calculation of the ground state of Be is made with an STO basis used earlier by Watson, but including s, p, and d orbitals only. The final 180-term CI expansion (1492 Slater determinants) gives an energy $E=-14.664193$ atomic units (a.u.) (Be), which is about 0.00221 a.u. higher than a nonrelativistic estimate for this state, and the pair energies $\epsilon(1s,1s)=-0.040869$ a.u., $\epsilon(2s,2s)=-0.045104$ a.u., and $\epsilon(1s,2s)=-0.005240$ a.u., are in excellent agreement with those found by Kelly by means of a many-body perturbation calculation, and also by Byron and Joachain, who used a variation-perturabtion method. Quantitative comparisons with all previous work on Be are made. Single excitations occur with large eigenvector components, but they become vanishingly small when NO's of the final wave function are used as the basis. The eigenvector components of quadruply excited configurations are closely related to those arising from a separated-electron-pair wave function without the strong orthogonality condition. The spd energy limit is estimated to be $E_{spd}=-14.66453$ a.u. From considerations *not* involving relativistic corrections, the "exact" nonrelativistic energy is estimated to be lower than $E=-14.66639$ a.u. by no more than 0.0003 a.u. The "exact" pair energies are estimated to be $\epsilon(1s,1s)=-0.04261$ a.u., $\epsilon(2s,2s)=-0.04550$ a.u., and $\epsilon(1s,2s)=-0.00530$ a.u. Details on all aspects of the calculation are given. Further work on several states of the first-row atoms is in progress.

I. INTRODUCTION

THE simplest and most general variational method in connection with numerical applications to the stationary states of many-electron systems is the configuration-interaction (CI) method.[1,2] When the CI expansion is truncated to only one term (configuration) and the total electronic energy is minimized with respect to some well-defined sort of variations of the spin orbitals, we have a particular kind of Hartree-Fock (HF) method.[3,4] In conventional HF calculations, the spin orbitals are understood to be symmetry adapted, and the configuration is chosen to be a projected Slater determinant of the required symmetry.[5]

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[1] E. A. Hylleraas, Z. Physik **48**, 469 (1928); S. F. Boys, Proc. Roy. Soc. (London) **A201**, 125 (1950). See also E. A. Hylleraas, *Abhandlungen aus den Jahren 1926–37* (Oslo University Press, Oslo, 1956).

[2] P. O. Löwdin, Phys. Rev. **97**, 1474 (1955).

[3] P. O. Löwdin, Phys. Rev. **97**, 1490 (1955).

[4] R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, 312 (1955); R. K. Nesbet, Rev. Mod. Phys. **33**, 28 (1961).

[5] C. C. J. Roothaan, Rev. Mod. Phys. **23**, 69 (1951); **32**, 179 (1960); C. C. J. Roothaan and P. Bagus, in *Methods in Computational Physics* (Academic Press Inc., New York, 1963), Vol. 2.

In the present series of nonrelativistic atomic calculations we perform CI with projected Slater determinants, including the conventional HF configuration. We use a symmetry-adapted[4] one-electron orthonormal basis whose radial part is expanded in terms of Slater-type orbitals (STO's). When a configuration is degenerate with respect to the LS term under consideration [e.g., the configuration $(p)^2(d)^2$ is triply degenerate with respect to ^1S states], the full degenerate space is taken into account, without giving any *a priori* preferences to a particular coupling of the spin and orbital angular momentums.

The method commonly used by other authors has been to build up a wave function by successive addition of appropriate configurations to an already determined approximation, and sometimes by even optimizing the STO parameters with respect to the total energy. As a first step in the determination of CI wave functions, we take the opposite stand: An STO basis is chosen *a priori* with the only requisite that approximate linear dependencies be within the limits of accuracy imposed. It is desirable, although not necessary, that a good HF wave function be obtainable from such a basis.

Since the variational energy of the full CI expansion depends on the STO basis alone, one of our tasks is to devise a strategy to find an orbital basis leading to a rapid convergence of the CI expansion. This is attempted by taking the natural orbitals (NO's)[2,6] of a CI wave function which includes the HF configuration and all possible double excitations of it, such that the HF orbitals remain NO's. Conceptual and practical justifications for doing so are given in Sec. II.

The second step consists of carefully building up the STO basis from the NO's obtained in the first step; this shall be considered in a forthcoming paper dealing with more accurate calculations on the ground states of the Be isoelectronic series. There is no practical motivation for not carrying out this second step right after the first one, and, in fact, this is the course we are following in further calculations. However, we are considering here only the first step in order to concentrate on the question: What is the best one can do with a given STO basis? The answer to this question (which is not trivial when a full CI treatment is out of range) should obviously precede any estimates on the actual rate of convergence of CI expansions in a one-electron basis.

We have two reasons for adopting this approach: Firstly, it is of interest to know the relative importance of spending large amounts of computing time in doing a careful optimization of STO parameters; secondly, large Hamiltonian matrices can be generated very fast—a 185×185 matrix for the ground state of carbon, including 1800 Slater determinants, is computed in 24 sec on a CDC 6400 computer—and thus there should be no real hindrance to an exhaustive search aiming at determining which configurations contribute effectively to the CI expansion.

The ground state of Be is computed with the same STO basis employed previously by Watson,[7] except that we consider s, p, and d orbitals only. The STO choice is dictated in part because much work and thought has been given to Watson's wave function in the years since its publication, and thus we have enough material to make comparisons and draw evidence on the usefulness of this method. In Sec. III we give a brief account of the calculation. The results are presented in Sec. IV and discussed in Sec. V.

II. ORBITAL BASIS

Among the general studies aiming at improving the rate of convergence of the many-electron CI expansion,[2,8,9] the concept of natural orbitals plays an important role. Multiconfiguration self-consistent-field (SCF) theories[8] are currently being applied to many molecular and atomic systems, but since no real effort seems to be made to obtain good atomic wave functions by these methods, nothing can be said at present about their practical convenience in atomic calculations.[10]

Natural orbitals have been offered as a panacea to speed up the convergence of the exact CI expansion.[2,6,11] In the case of approximate wave functions, the (approximate) NO's are supposed to simplify the approximate CI expansion. Applications to two-electron systems speak eloquently of the success of NO analyses[12,13]; all these have been done with approximate NO's. The equations to derive the *exact* NO's require the knowledge of the exact second-order density matrix.[2] Approximate solutions, however, can be obtained for

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[6] P. O. Löwdin, Rev. Mod. Phys. **32**, 328 (1960).

[7] R. E. Watson, Phys. Rev. **119**, 170 (1960).

[8] (a) A. P. Yutsis, Zh. Eksperim. i Teor. Fiz. **23**, 129 (1952) (English translation on request from Photo Duplication Service, Publication Board Project, Library of Congress, Washington, D.C. 20025); J. C. Slater, Phys. Rev. **91**, 528 (1953); R. McWeeny, Proc. Roy. Soc. (London) **A232**, 114 (1955); T. L. Gilbert, J. Chem. Phys. **43**, S248 (1965); G. Das and A. Wahl, *ibid.* **44**, 87 (1966); A. Veillard, Theoret. Chim. Acta **4**, 22 (1966); E. Clementi and A. Veillard, *ibid.* **7**, 133 (1967); J. Hinze and C. C. J. Roothaan, Laboratory of Molecular Structure and Spectra Report, Department of Physics, University of Chicago (unpublished); W. H. Adams, Phys. Rev. **156**, 109 (1967); see also Ref. 2. (b) P. O. Löwdin, J. Math. Phys. **3**, 1171 (1962), and references therein.

[9] W. Kutzelnigg, Theoret. Chim. Acta **1**, 327 (1963); W. Kutzelnigg, J. Chem. Phys. **40**, 3640 (1964).

[10] For applications to two- and four-electron atoms see A. P. Yutsis *et al.*, Opt. i Spektroskopiya **12**, 157 (1962) [English transl.: Opt. Spectry. (USSR) **12**, 83 (1962)]. Impressive results are claimed for Be. However, the fact that the HF energy reported by these authors is 0.0040 a.u. lower than the correct value, leads one to suspect that at least the same errors are involved in the final energies. This probably has to do with innaccuracies in the numerical integrations.

[11] P. O. Löwdin, J. Phys. Chem. **61**, 55 (1957).

[12] H. Shull and P. O. Löwdin, J. Chem. Phys. **30**, 617 (1959).

[13] E. R. Davidson and L. L. Jones, J. Chem. Phys. **37**, 2966 (1962); S. Hagstrom and H. Shull, Rev. Mod. Phys. **35**, 624 (1963), to name a few. For accurate NO's in the He isoelectronic series see Ref. 43.

two-electron systems.[14] Atomic and molecular calculations on systems with more than two electrons, in which approximate NO's are used in different ways in the determination of the wave functions, have recently been carried out.[15,16] In what follows we apply NO ideas to the determination of a Be ground-state wave function.

Let us now return to the two-electron problem: Löwdin and Shull consider the mean quadratic deviation between a CI expansion of a two-electron wave function and a truncation of the same function,[17] and prove that this quantity is a minimum for the case of the natural expansion, when the latter, ordered according to decreasing occupation numbers, is truncated to any given order.[18] As these authors point out, the preceding situation results as a consequence of diagonalizing a quadratic form. We shall use this fact in the following context: A four-electron separated-electron-pair wave function Ω,

$$\Omega=A\{K(1,2)L(3,4)\}\,, \tag{1}$$

has been shown to be a very good approximation to the ground state of Be.[19,20] We assume then, that an essentially correct $K(1,2)$ function which is presumably localized in the K shell can be obtained by letting the L-shell wave function be $(2s)^2$, i.e., a doubly occupied $2s$ orbital. The function $K(1,2)$ is expanded in CI form and its NO's are called *K-shell NO's*. The truncated natural expansion of $K(1,2)$ has optimum properties: a minimum mean quadratic deviation with respect to the original $K(1,2)$, or what is equivalent, maximum overlap with it. In this way, a large basis can be effectively reduced. Let us note here that we are not looking for a basis to represent $K(1,2)$ in an optimum way, but rather for a good basis in which to expand that localized portion of the total wave function, the "physical" K shell, in the general framework of an unrestricted CI calculation.

Since all the basis orbitals are orthogonal, the NO's of $K(1,2)$ are identical with those of $\Omega^{(K)}$,

$$\Omega^{(K)}=A\{K(1,2)(2s)^2\}\,,$$

except for the addition of two $2s$ spin orbitals with occupation number (o.n.) equal to 1.

The L-shell NO's can be found in a similar way, in which case $K(1,2)$ is represented by $(1s)^2$. The K-shell NO's are not exactly orthogonal to their L-shell counterpart. Orbitals obtained in exactly the same way have been used in molecular calculations by Bender, Davidson, Edmiston, and Krauss.[15]

In order to avoid the nonorthogonality problem, the function $\Omega^{(KL)}$ is considered:

$$\Omega^{(KL)}=(1s)^2(2s)^2+A\{[\sum_{i\leq j}{}^{1S}(x_ix_j)k_{ij}](2s)^2\}+A\{(1s)^2[\sum_{i\leq j}{}^{1S}(x_ix_j)l_{ij}]\}\,, \tag{2}$$

and it is found that its NO's resemble either K-shell NO's or L-shell NO's[16]; we shall call them *KL-shell NO's*. In addition, we now impose constraints upon Eq. (2) to the effect that the HF orbitals remain NO's[21]; thus all single excitations in the four-electron CI expansion are omitted when calculating the KL-shell NO's. In this way, we obtain an orthogonal set which includes the HF orbitals intact.

The resemblance between the KL-shell NO's and either the K- or L-shell NO's, seems to be greater when the former ones include the HF orbitals, as is the case in the present calculation. Moreover, this is not a restriction; in fact we have carried out similar calculations using the "ground" NO's of a very accurate CI wave function instead of the HF orbitals, and the convergence of the CI expansion is found to be as good as the one in the present work. However, since we work with HF orbitals, our calculated pair energies are comparable with those found by other methods (Table VI).

The K- and L-shell NO's are important in order to know how many orbitals of a given symmetry type are energetically effective for describing a given shell (smaller energy contributions with decreasing o.n.'s).

On the other hand, the KL-shell NO's are used as a basis for an unrestricted CI calculation. Their o.n.'s provide a criterion for the classification of the orbitals. Thus, $1s$ will now be called s_1 because it occurs with the largest o.n. among the s-symmetry NO's of the KL-shell CI wave function. Analogously, s_4 refers to the KL-shell NO with the fourth largest o.n. of s symmetry, and so on. The o.n.'s of these NO's do not give a relative in-

TABLE I. STO parameters.

Value of j:	1	2	3	4	5	6	7	8	9
Value of n_j:	0	0	1	1	2	2	3	3	4
Z_{j1}	6.0	1.0	6.0	1.0	6.0	1.0	6.0	1.0	6.0
Z_{j2}	9.0	1.5	9.0	1.5	9.0	1.5	9.0		
Z_{j3}	12.0	2.0	12.0	2.0	12.0				

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[14] C. E. Reid and Y. Ohrn, Rev. Mod. Phys. **35**, 445 (1963); W. Kutzelnigg, Theoret. Chim. Acta **1**, 343 (1963). The work of E. R. Davidson [J. Chem. Phys. **39**, 875 (1963)] deserves special mention. See also R. Ahlrichs, W. Kutzelnigg, and W. A. Bingel, Theoret. Chim. Acta **5**, 289 (1966).

[15] C. F. Bender and E. R. Davidson, J. Phys. Chem. **70**, 2675 (1966); C. Edmiston and M. Krauss, J. Chem. Phys. **45**, 1833 (1966); C. F. Bender and E. R. Davidson, *ibid*. **47**, 360 (1967).

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[17] P. O. Löwdin and H. Shull, Phys. Rev. **101**, 1730 (1956).

[18] A. J. Coleman, Rev. Mod. Phys. **35**, 668 (1963), see in particular p. 672.

[19] T. L. Allen and H. Shull, J. Phys. Chem. **66**, 2281 (1962); W. Kutzelnigg, Theoret. Chim. Acta **3**, 241 (1965); R. McWeeny and B. T. Sutcliffe, Proc. Roy. Soc. (London) **A273**, 103 (1963); D. W. Smith and S. J. Fogel, J. Chem. Phys. **43**, S91 (1965).

[20] K. J. Miller and K. Ruedenberg, J. Chem. Phys. **43**, S88 (1965).

[21] In Ref. 16 these constraints were not imposed, with the consequence that the KL shell NO's had to be reorthonormalized to the HF orbitals. In the few trials in which a departure from the HF orbitals was allowed, the rate of convergence was about the same as when the HF orbitals were conserved.

TABLE II. Orbital expansion coefficients in terms of STO basis.

				s-type orbitals			
j	s_1	s_2	s_3	s_4	s_5	s_6	s_7
1	0.484847048	−0.081129323	0.236378724	−0.851510600	0.265873679	−1.664939862	1.747779195
2	0.217606868	−0.147345521	−0.023812423	1.463671983	−13.785058233	8.345092690	−7.846111097
3	0.264166060	−0.051149614	0.167902301	−0.685884011	0.344405362	−1.322541330	−0.884531760
4	−0.268301860	1.332911822	−2.906858860	−4.155520278	19.479361764	−8.963389965	21.059262690
5	0.168224986	−0.041063909	−0.013116037	1.445011855	5.662577867	6.664641564	−4.337304547
6	0.167584376	−0.386780254	3.543805952	3.499072719	−11.287118625	2.486636455	−22.934860600
7	0.045127695	−0.007522402	−0.086177264	−0.217448010	−4.044845351	−9.770113013	12.217441615
8	−0.045287495	0.224825231	−0.597044312	−0.735281328	1.832170487	0.929981389	9.551494834
9	0.066882692	−0.027648005	0.170930863	0.272415025	2.913346819	1.996914822	−7.890760494
				p-type orbitals			
j	p_1	p_2	p_3	p_4	p_5	p_6	p_7
1	0.002277605	0.136828110	−0.038576770	0.446091524	0.772159722	−1.158594603	−8.047062883
5	0.429793323	0.289757091	−2.297429706	−1.630546141	3.711662087	9.027008344	−5.030483716
3	−0.008093853	0.496375468	−0.064288357	1.093397758	2.043059686	−1.562780864	25.023119574
4	0.003407640	−0.484820859	6.516898324	3.221044478	−5.988190796	−13.135420198	6.885709737
5	0.018387890	−0.015723759	−0.025078480	−0.466722842	−6.118314509	7.467695431	−30.069575113
6	0.639694745	0.061136712	−4.653924469	−1.709415789	2.804971927	5.851017849	−2.951912363
7	−0.017083311	0.395753639	0.268955253	−0.793415524	2.983994709	−7.299083802	14.311612643
				d-type orbitals			
j	d_1	d_2	d_3	d_4			
1	0.023051110	0.227546159	−0.163580523	5.623365897			
2	−0.642843178	0.114330993	0.011583282	0.564588369			
3	−0.069167477	−0.155445203	−2.845782094	−10.450285207			
4	1.574948229	−0.118129593	−0.028951140	−0.500672470			
5	0.087376028	0.949263475	2.905383969	5.354361470			

dication of the energy effects of their corresponding NO's in a CI expansion. For example, the orbital d_1 is largely an L-shell NO, but it is energetically poor when compared with d_2, a predominantly K-shell NO. The energy contributions of d_2 are three times as large as those of d_1,[22] while the o.n. of d_1 is five times that of d_2.[23]

More about KL-*shell NO's* is said in Sec. III C. We mention here two practical advantages: Firstly, it is found in practice that when the approximate linear dependencies are not serious, the NO's resemble canonical orbitals.[24] As a consequence, one- and two-electron integrals can be computed with a nearly optimum accuracy. Secondly, the Hamiltonian matrix in NO basis usually occurs with a more dominant diagonal, and as a result of this, iterative methods for obtaining eigenvalues and eigenvectors[25] converge much faster. In similar calculations on the carbon atom, speed improvements by a factor of 6 have been observed.[26]

III. CALCULATION

The computer programs, which are general for any *LS* state of any atom, were written in FORTRAN IV on the basis of programs earlier developed by the present author.[16] The actual calculations were performed on a 32K, CDC 6400 computer at Florida State University.[27]

A. One-Electron Basis

The set of spin orbitals $\Phi_{ilm_lm_s}$ is defined by

$$\Phi_{ilm_lm_s}=R_{il}(r)\cdot Y_{lm_l}(\theta,\varphi)\xi_{m_s}(\sigma_s)\,,$$

where $\{Y_{lm_l}\}$ consists of normalized spherical harmonics in the Dirac phase convention[28] and $\{\xi_{m_s}(\sigma_s)\}$ are the usual spin functions α, β with eigenvalues $m_s=\pm\frac{1}{2}$. The set of functions $\{R_{il}\}$ is expanded in terms of normalized STO's S_{jl} with $j=1,\cdots,J(l)$:

$$R_{il}=\sum_{j}^{J(l)} S_{jl}a_{jli}\,,$$

$$S_{jl}=N_{jl}r^{(n_j+l)}e^{-Z_{jl}r}\,,$$

$$N_{jl}=[(2Z_{jl})^{[2l+2n_j+3]}/(2l+2n_j+2)!]^{1/2}\,,$$

and we have further the orthonormalization condition

$$\int_0^\infty R_{il}(r)R_{jl}(r)r^2dr=\delta_{ij}\,.$$

The STO parameters are given in Table I, the expansion coefficients a_{jli} in Table II. All one-electron integrals are computed in 2 sec for a 7*s*, 7*p*, 4*d* basis; this includes a Schmidt orthonormalization of the orbital basis. It takes 55 sec to compute all two-electron

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[22] A fact already known; see J. Linderberg and H. Shull, J. Mol. Spectry. **5**, 1 (1960).

[23] All this can be suspected just by looking at Watson's wave function (Ref. 7).

[24] These are orbitals for which the sum of the squared modulus of their expansion coefficients in terms of a nonorthogonal basis is a minimum; see, e.g., P. O. Löwdin, J. Appl. Phys. **33**, 251 (1962).

[25] See, in particular, R. K. Nesbet, J. Chem. Phys. **43**, 311 (1965). A computer program has been written in FORTRAN IV by H. H. Michels and P. Elliot and may be obtained as QCPE 93 from Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, Bloomington, Indiana.

[26] A. Bunge (unpublished calculations on the C atom).

[27] A double precision arithmetic (25 figures) recomputation was carried out on a 64K CDC 3600/3400 computer at Indiana University.

[28] $Y_{lm}^*=(-1)^mY_{l,-m}$.

TABLE III. Nondegenerate configurations.

Subclass	General element
1	$(s_w s_x \mid s_w s_x)$
2	$2^{1/2}O(s_w s_x \mid s_w s_y)$
3	$3^{1/2}O(sp^0 \mid sp^0)$
4	$6^{1/2}O(sp_w{}^0 \mid sp_x{}^0)$
5	$6^{1/2}O(s_w p^0 \mid s_x p^0)$
6	$3^{1/2}O(p^0 p^1 \mid p^{\bar{1}} p^0)$
7	$12^{1/2}O(p_w{}^0 p_w{}^1 \mid p_w{}^0 p_x{}^{\bar{1}})$
8	$5^{1/2}O(sd^0 \mid sd^0)$
9	$10^{1/2}O(sd_w{}^0 \mid sd_x{}^0)$
10	$10^{1/2}O(s_w d^0 \mid s_x d^0)$
11	$15^{1/2}O(sp^0 \mid p^0 d^0)$

radial integrals over $9s$, $7p$, $5d$ STO basis. These are computed once and for all. It takes another 60 sec to make the transformation to an orthogonal set of $7s$, $7p$, and $4d$ orbitals.

B. CI Expansion

The total wave function Ψ is expanded as

$$\Psi = \sum_{K,p} \Phi_K{}^{(p)} a_{Kp},$$

where

$$\Phi_K{}^{(p)} = O(L^2,S^2)\left[\sum_{\alpha=1}^{p} D_{K\alpha} b_{K\alpha}{}^{(p)}\right] = \sum_{\alpha=1}^{n_K} D_{K\alpha} c_{K\alpha}{}^{(p)}. \quad (3)$$

In Eq. (3), $O(L^2,S^2)$ is a product of a spin-angular-momentum projection operator times an orbital-angular-momentum projector,[29] and it is taken to be idempotent. In the Slater determinant $D_{K\alpha}$, the α's label the possible determinants in configuration K [a configuration is defined by the ordered set of all (i,l) numbers which participate in a given determinant]. Some configurations allow for only one linearly independent projected function corresponding to a given set of L, L_z, S, S_z values. Such configurations are called nondegenerate. When more than one linearly independent function can be obtained, these functions are called degenerate and are labeled by the superscript p. The successive elements of the degenerate set are obtained by Schmidt orthogonalization of $O(L^2,S^2)D_{Kp}$ to the previous elements.

The matrix elements $H_{KJ}{}^{(pq)}$ are given by[30]

$$H_{KJ}{}^{(pq)} = \langle \Phi_K{}^{(p)} | H | \Phi_J{}^{(q)} \rangle$$

$$= \sum_{\alpha=1}^{p} \sum_{\beta=q}^{n_J} b_{K\alpha}{}^{(p)} c_{J\beta}{}^{(q)} \langle D_{K\alpha} | H | D_{J\beta} \rangle,$$

and the "turnover" rule is applied in such a way that the number of matrix elements between Slater determinants is kept to a minimum.

The types of configurations which occur in the final wave function are displayed in Tables III and IV. In the normalized Slater determinant $(i_w{}^a j_x{}^b | k_y{}^c l_z{}^d)$, the letters i, j, k, l stand for the l quantum number, the superscripts stand for the quantum number m_l, and the subscripts for the quantum number i. In these tables the later are included to distinguish between groups of equivalent electrons. Regarding phase conventions, it is understood that among orbitals of the same symmetry $z>y>x>w$. Finally, the orbitals to the left of the bar are associated with α spin ,those to the right with β spin.

C. *KL*-Shell CI

Since the set of STO's employed has very serious linear dependencies, it is necessary to carry out 25 figures in the arithmetic operations. The occurrence of approximate linear dependencies can be diagonosed in several ways, but a fruitful one is as follows: A linear transformation upon the basis of symmetry orbitals must leave the energy of a *KL*-shell CI invariant because this wave function is invariant under the same transformation. If the energy changes after such transformations, one must reduce the size of the STO basis, or modify it. Some times this is not necessary and a reduction in the size of the orbital basis alone is sufficient to keep the errors within the desired bounds.

D. Choice of Configurations

All possible types of configurations are examined. An eigenvector criterion is imperative for the selection of configurations if, in addition to obtaining a good energy,

TABLE IV. Degenerate configurations.

Subclass	First element	Second element	Third element
12	$(3)^{1/2}O(s_w s_y \mid s_x s_z)$	$O[-(s_w s_y \mid s_x s_z)+2(s_w s_x \mid s_y s_z)]$ [a]	
13	$3O(s_w p_x{}^0 \mid s_y p_z{}^0)$	$(3)^{1/2}O[-(s_w p_x{}^0 \mid s_y p_z{}^0)+2(s_w p_z{}^0 \mid s_y p_x{}^0)]$	
14	$(15/2)^{1/2}O(p_w{}^0 p_x{}^1 \mid p_w{}^0 p_x{}^{\bar{1}})$	$(9/10)^{1/2}O[(p_w{}^0 p_x{}^1 \mid p_w{}^0 p_x{}^{\bar{1}})+4(p_w{}^1 p_x{}^0 \mid p_w{}^0 p_x{}^{\bar{1}})]$	$(6/10)^{1/2}O[-(p_w{}^0 p_x{}^1 \mid p_w{}^0 p_x{}^{\bar{1}})$ $-4(p_w{}^1 p_x{}^0 \mid p_w{}^0 p_x{}^{\bar{1}})+5(p_w{}^0 p_w{}^1 \mid p_x{}^{\bar{1}} p_x{}^0)]$
15	$(15)^{1/2}O(p_w{}^0 p_y{}^1 \mid p_w{}^0 p_x{}^{\bar{1}})$ [b]	$(9/5)^{1/2}O[(p_w{}^0 p_y{}^1 \mid p_w{}^0 p_x{}^{\bar{1}})+4(p_w{}^1 p_y{}^0 \mid p_w{}^0 p_x{}^{\bar{1}})]$	
16	$(15)^{1/2}O(s_w d_x{}^0 \mid s_y d_z{}^0)$	$(5)^{1/2}O[-(s_w d_x{}^0 \mid s_y d_z{}^0)+2(s_w d_z{}^0 \mid s_y d_x{}^0)]$	
17	$(105/11)^{1/2}O(p^0 d^0 \mid p^0 d^0)$ [b]	$(60/11)^{1/2}O[-(p^0 d^0 \mid p^0 d^0)+11/6(p^{\bar{1}} d^1 \mid p^{\bar{1}} d^1)]$	

[a] This function is equal to $-A[(s_w|s_y)+(s_y|s_w)][(s_x|s_z)+(s_z|s_x)]$; e.g., it corresponds to an antisymmetrized product of two ^1S two-electron functions.
[b] Triply degenerate configuration; only two elements occur in the final wave function.

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[29] P. O. Löwdin, Rev. Mod. Phys. **36**, 966 (1964).

[30] P. O. Löwdin, Rev. Mod. Phys. **34**, 520 (1962).

TABLE V. Comparison of angular energy limits.

	s[a]	sp	spd	$spdf$	$spdfg$	E(total)
Watson[b]	−14.5865	−14.6534	−14.6566	−14.65724	−14.65740	
Weiss[c]	−14.59110	−14.65722	−14.66039	−14.66090		
MR[d]	···	···	−14.6612	−14.66179		
Bunge[e]	−14.59073	−14.65923	−14.66213			
This calc.	−14.59202	−14.66080	−14.66419			
Nonrelativistic estimate			−14.66453[f]	−14.66570[f]	−14.66598[f]	−14.66639[f] −14.66743[g] −14.667306[h] −14.666917[i]

[a] All energies in this paper are in a.u. (Be).
[b] Reference 7.
[c] Reference 33.
[d] Reference 34.
[e] Reference 16.
[f] Upper bounds estimated in this work, deduced from Tables XV and XVI.
[g] C. W. Scherr, J. N. Silverman, and F. A. Matsen, Phys. Rev. **128**, 2675 (1962).
[h] Reference 37.
[i] Reference 38, based on an uncertain experimental value for the total energy of the Be ground state; see Refs. 7 and 37.

one is interested in a good wave function. The magnitude of the eigenvector components which may be neglected without affecting the energy decreases with increasing nuclear charge Z, within the family of configurations which contribute to the expansion of a given pair of electrons. Also, the eigenvector components for configurations which correlate outer electrons are larger than those that correlate electrons closer to the nucleus, when the energy contributions are the same.

The search for energy limits of *classes* is also considered. A *class* is defined by the number of orbitals of each l value which occur in a given configuration. Thus, the *subclasses* $(s)^2(p)^2$, $s_ws_x(p)^2$, $(s)^2p_wp_x$, and $(s_ws_xp_yp_z)$ belong to the same class $(2s,2p)$. Class energy limits are useful because they are invariant under a nonsingular linear transformation of the basis of symmetry orbitals.

In addition, partial energies (p.e.)[31,32] and second-order perturbation-theory (SOPT) estimates of energy contributions are computed every time. Partial energy contributions are found to be very useful when instead of the HF configuration, a selected CI wave function is used as zeroth-order approximation. The selected CI wave function is taken to include those configurations with higher eigenvector components. The final wave function reported here was obtained after examining about 1000 configurations and keeping those functions with eigenvector components larger (in absolute value) than 0.0009, and corresponding partial energy contributions larger than 0.0001 a.u. This is done by the CDC

TABLE VI. Comparison of pair energies and total correlation energy.

	$\epsilon(1s,1s)$	$\epsilon(2s,2s)$	$\epsilon(1s,2s)$	E_{corr}
Kelly[a]	−0.04212	−0.04488	−0.004966	−0.09197
BJ[b]	−0.04247	−0.04482	−0.00524	−0.09253
This calc.[c]	−0.040869	−0.045104	−0.005240	−0.091612
"Exact"[c,d]	−0.04261	−0.04550	−0.00530	−0.09341
Nesbet[e]	(−0.041827)	(−0.045351)	(−0.005864)	(−0.092050)
SB[f]	(−0.04235)	(−0.04450)	···	···
This calc.[g]	(−0.040926)	(−0.045669)	···	···
"Exact"[h]	(−0.04267)	(0.04607)	···	···
TS[i]	((−0.04395))	((−0.04392))	((−0.00648))	((−0.09435))
GTL[j]	((−0.042083))	((−0.044381))	···	···

[a] Reference 35; HF orbitals taken from V. V. Kibartas andA. P. Yutsis [Zh. Eksperim. i Teor. Fiz. **25**, 264 (1953)] which report $E_{\text{HF}}=-14.578$ a.u. a certainly inaccurate value, probably due to round-off errors in the numerical integrations. See also V. V. Kibartas, V. I. Kavetskis, and A. P. Yutsis, Zh. Eksperim. i Teor. Fiz. **29**, 623 (1955)] [English transl.: Soviet Phys.—JETP **2**, 476 (1956)].
[b] Reference 39; $E_{\text{HF}}=-14.57302$.
[c] With respect to an $E_{\text{HF}}=-14.572986$.
[d] This work, Table XVI.
[e] Reference 38.
[f] Reference 40.
[g] Calculated with orbital basis employed in this work.
[h] Corrections taken from Table XVI.
[i] Reference 36; $E_{\text{HF}}=-14.572347$.
[j] Reference 37; $E_{\text{HF}}=-14.572956$.

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[31] A partial energy $(\text{p.e.})_i$ contribution is defined by (Ref. 32) $(\text{p.e.})_i=c_iH_{i0}/c_0$, where the c's are eigenvector components, the subscript zero being associated with any zeroth-order function. If the c's are variational coefficients, the energy of the zeroth-order wave function plus the sum of the p.e.'s equals the total energy. Pair energies result from addition of p.e.'s over a given type of pair excited configurations.

[32] See Boys's paper, Ref. 1.

3400/3600 computer in 75 min, of which 55 min are spent in getting eigenvalues and eigenvectors, 13 min in constructing Hamiltonian matrices, 1 min building up a magnetic tape with all determinants, projection coefficients, and Gaunt coefficients, and 6 min are spent in the handling of magnetic tapes; integrals are given as input. All excluded configurations with significant p.e.'s are considered in the expansion of the final wave function. In this case we took into account most of the functions with p.e.'s greater than 0.000002 a.u.

TABLE VII. Effect of $(s_1)^2$ excitations.

Configuration[a]	Eigenvector[b]	Partial energies[c]	Eigenvector Be^{++}[d]
$(p_2)^2$	-0.028518606	-20299^{e}	-0.0285
$(s_4)^2$	-0.016776555	-7868^{e}	-0.0167
s_3s_4	$+0.013873568$	-3937^{e}	$+0.0141$
p_1p_2	-0.008497118	-1093^{e}	-0.0084
$(s_3)^2$	-0.006472686	-623^{e}	-0.0069
$(d_2)^2$	-0.006377440	-2647^{e}	-0.0063
$(p_4)^2$	-0.005114480	-1949^{e}	-0.0051
p_3p_4	$+0.001933950$	-125^{f}	$+0.0018$
s_5s_6	-0.001850151	-274	-0.0018
$(s_5)^2$	-0.001830927	-177	-0.0018
$(d_3)^2$	-0.001749529	-435	-0.0018
p_1p_4	$+0.001663548$	-82	$+0.0016$
$(p_5)^2$	-0.001514453	-254	-0.0014
$(s_6)^2$	-0.001363750	-174	-0.0013
s_4s_5	-0.001171144	-69	-0.0012
$(p_1)^2$	-0.001074516	-13	-0.0016
s_3s_5	-0.000921051	-22	-0.0009
p_1p_3	-0.000778436	-8	-0.0006
s_3s_6	-0.000640354	-20	-0.0008
$(s_7)^2$	-0.000599537	-25	-0.00059
$(p_6)^2$	-0.000561004	-43	-0.00054
$(p_3)^2$	-0.000535401	-7	-0.00047
p_1p_5	-0.000469536	$+5$	-0.00046
s_6s_7	$+0.000461944$	-38	$+0.00047$
$(d_4)^2$	-0.000461803	-82	-0.00046
p_5p_6	$+0.000359381$	-48	$+0.00042$
p_3p_5	-0.000358717	$+10$	-0.00037
$(p_7)^2$	-0.000327412	-52	-0.00032
p_2p_4	-0.000326783	-6	-0.00038
d_2d_3	-0.000269289	$+4$	-0.00031
d_1d_2	-0.000256070	-2	-0.00030
p_4p_5	-0.000208527	-14	-0.00031
s_5s_7	-0.000199317	$+10$	-0.00017
d_3d_4	-0.000119923	$+14$	-0.00012
s_4s_6	-0.000115479	-5	-0.00014
p_6p_7	-0.000110332	-12	-0.00011
p_2p_3	$+0.000090040$	-2	$+0.00016$
p_5p_7	-0.000046812	$+4$	-0.00005

[a] Only the excited orbitals are shown, e.g., the configuration $(s_2)^2(p_2)^2$ is denoted simply by (p_2^2).

[b] The eigenvector component of the HF configuration is $c_0(\mathrm{Be}) = +0.953115148$. The eigenvector is normalized in the sense $\langle\Phi_0|\Psi\rangle = 1$, where Φ_0 is a selected CI wave function (see Sec. III D and footnote e below) which is normalized to 1, and Ψ is our total wave function.

[c] In units of 10^{-6} a.u. (Be).

[d] Eigenvector components multiplied times $[c(\mathrm{Be})/c_0(\mathrm{Be}^{++})]^2$ where $c(\mathrm{Be})^2$ is the sum of all squared coefficients of configurations which are not $(s_1)^2$ excitations.

[e] Partial energies defined by $\Phi_0 = \Phi_{\mathrm{HF}}$.

[f] Partial energies defined by a selected CI wave function Φ_0 which is made up of all configurations marked above, and others similarly indicated in the following tables. The same applies to all configurations below. The energy corresponding to Φ_0 is $E = -14.658278$ a.u.

IV. RESULTS

The energy results obtained with a 180-term wave function (WF1), consisting of 1492 Slater determinants, are tabulated in Table V and compared with previous variational calculations.[7,16,33,34] It should be emphasized that our calculated energies are a byproduct of a calculation with a fixed STO set (first step in the determination of CI wave functions, Sec. I). When the NO's of WF1 are employed as a basis, we obtain a different representation of WF1, which we shall call WF2. The latter consists of 179 terms and gives the same energy as WF1. When the terms with partial energies smaller than 0.000020 a.u. are discarded, we obtain a 91-term expansion with an energy $E = -14.66372$ a.u. in the case of WF1, and an 85-term expansion with an energy $E = -14.66381$ a.u. in the case of WF2. The above results, together with a comparison of WF1 and WF2 which we have omitted here, show that the *KL*-shell NO's provide an orbital basis as reliable as a good NO basis.

The last row in Table V exhibits the estimates for the *spd* and higher angular energy limits, as deduced in Sec. V.

The energy breakdown into different kinds of pair energies is displayed in Table VI and compared with previous calculations.[35–40] Our pair energies are defined relative to the HF function we employed, namely, Watson's.

Kelly applies many-body perturbation theory (infinite-order perturbation theory) and uses an *spd* basis.[35] Byron and Joachain (BJ), instead, apply Rayleigh-Schrödinger perturbation theory through second order in the wave function (fifth order in the energy), including enough higher *l* orbitals to ensure convergence within reasonable limits.[39] Both kinds of perturbation theory and the CI method must give the same pair energies when carried out far enough in accuracy, if the same zeroth-order approximation is employed, e.g., Hartree-Fock.

On the other hand, Nesbet's pair energies,[38] as well as Szasz and Byrne's (SB),[40] are both defined in terms of a complete doubly excited (and singly excited) CI with respect to an HF basis, and thus they do not add up to the total correlation energy. In order to be able to make comparisons with their results, we have calculated the

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[33] A. W. Weiss, Phys. Rev. **122**, 1826 (1961).

[34] K. J. Miller and K. Ruedenberg, reports, Institute for Atomic Research, Department of Chemistry, Iowa State University (unpublished); see also J. Chem. Phys. (to be published).

[35] H. P. Kelly, Phys. Rev. **131**, 684 (1963); **136**, B896 (1964). Kelly uses a.u. and not a.u.(Be). For applications to open shell systems see H. P. Kelly [*ibid.* **144**, 39 (1966)] and an article in *Perturbation Theory and its Applications*, edited by C. H. Wilcox (John Wiley & Sons, Inc., New York, 1966).

[36] D. F. Tuan and O. Sinanoglu, J. Chem. Phys. **41**, 2677 (1964).

[37] M. Geller, H. S. Taylor, and H. B. Levine, J. Chem. Phys. **43**, 1727 (1965).

[38] R. K. Nesbet, Phys. Rev. **155**, 51 (1967).

[39] F. W. Byron and C. J. Joachain, Phys. Rev. **157**, 7 (1967).

[40] L. Szasz and J. Byrne, Phys. Rev. **158**, 34 (1967).

TABLE VIII. Effect of $(s_2)^2$ excitations.

Configuration[a]	Eigenvector[a]	Partial energies[a]
$(p_1)^2$	−0.293305851	−40942[b]
$(s_3)^2$	−0.039637156	−2325[b]
$(d_1)^2$	−0.016585658	−1415[b]
$(p_3)^2$	−0.006282298	−241[b]
s_3s_4	−0.005469578	+67[b]
$(s_4)^2$	−0.002638822	−77[c]
s_3s_5	−0.002150560	−30
$(s_5)^2$	−0.002128813	−20
s_4s_5	+0.002116239	+14
p_1p_3	−0.002066309	−7
p_3p_4	−0.001348507	−39
s_3s_6	+0.000878347	+6
s_5s_6	+0.000804758	+2
s_4s_6	−0.000612760	−6
p_2p_4	−0.000509901	−8
p_2p_3	+0.000472331	+2
p_3p_5	+0.000115128	+3

[a] See footnotes in Table VII.
[b] See footnote e in Table VII.
[c] See footnote f in Table VII.

latter pair energies also. For the two kinds of pair energies described so far, we have estimated the "exact" values, as shown in Sec. V.

Tuan and Sinanoglu (TS)[36] and Geller, Taylor, and Levine (GTL),[37] use interparticle coordinates in an application of Sinanoglu's many-electron theory.[41] Sinanoglu's theory assumes that the sum of the pair energies adds up to the total correlation energy (plus a small remainder) when HF orbitals are used for the ground configuration. It is not clear whether Sinanoglu's pair energies approach ours when the "small remainder" tends to zero.

Tables VII through XIV display the 180-term CI expansion. The K- and L-shell excitations can be accounted for by much shorter expansions than the ones shown in Tables VII and VIII, but the extra configurations have been included here because they have large eigenvector components and may therefore contribute to quantities other than the energy.

The intershell correlation expansion shown in Table IX is the largest one and it may be simplified also. Tables X and XI show the single excitations; their total energy effect, computed by eliminating them from the secular equation, amounts to −0.00058 a.u. When the NO's of the final wave function are used as a basis, both energy contributions and eigenvector components become vanishingly small, pointing out that the NO's of the Be ground state are closely related to the corresponding Brueckner orbitals.[8b]

Triple excitations are shown in Tables XII and XIII. Their total energy effect amounts to −0.00025 a.u.

The quadruple excitations, exhibited in Table XIV, seem to be similar to those arising from a separated-

TABLE IX. Effect of (s_1s_2) excitations.

Configuration[a]	Degenerate element[b]	Eigenvector[a]	Partial energies[a]
p_1p_2	1	+0.009298958	−909[c]
p_2p_3	2	+0.007739571	−671[c]
p_1p_2	2	−0.005832916	−407[c]
$(p_1)^2$		+0.005665796	−192[c]
$(s_4)^2$		−0.005526769	−665[c]
p_1p_4	1	−0.004910654	−176[c]
s_3s_4	1	+0.004260245	−209[d]
p_1p_3	1	+0.004135154	−73
p_2p_5	2	+0.004050267	−194
p_2p_4	2	−0.003969880	−384
s_3s_4	2	−0.003910590	−168
$(s_3)^2$		−0.003689154	−90
p_1p_5	1	+0.003497654	−348
p_3p_4	1	−0.003012166	−150
p_2p_6	2	+0.002410539	−27
p_1p_3	2	+0.002208640	−17
$(p_2)^2$		−0.002189112	−179
p_3p_5	1	+0.002185303	−13
p_2p_4	1	−0.002031486	−173
$(p_3)^2$		+0.001955324	−27
p_4p_5	2	−0.001882188	−101
p_1p_4	2	+0.001874173	−77
p_1p_6	1	+0.001818367	+52
p_3p_4	2	+0.001541513	−79
p_4p_6	2	−0.001236255	+4
s_3s_5	1	−0.001220236	+15
p_3p_6	1	+0.001088356	−2
$(d_1)^2$		+0.001008313	−6
p_2p_3	1	+0.001006345	−17
$(d_2)^2$		−0.000852915	−47
d_1d_2	1	+0.000765830	−12
s_4s_5	1	+0.000751988	−2
$(s_5)^2$		−0.000741167	−18
s_4s_5	2	+0.000664368	−12
p_5p_6	2	+0.000634820	−19
p_2p_5	1	+0.000633190	+14
s_5s_6	2	+0.000518236	−13
s_3s_5	2	+0.000495501	+7
p_4p_5	1	−0.000487776	−23
d_2d_3	2	+0.000478591	−26
p_1p_5	2	−0.000364804	+5
$(s_6)^2$		−0.000351517	−11
d_1d_2	2	−0.000343864	−3
p_3p_5	2	−0.000328715	+4
d_1d_3	1	+0.000315330	−3
s_3s_6	2	+0.000309802	+2
$(d_3)^2$		−0.000255805	−13
s_5s_6	1	−0.000233872	−7
$(p_5)^2$		+0.000229345	+8
d_2d_4	2	+0.000198398	−4
s_6s_7	2	−0.000179651	−3
$(s_7)^2$		−0.000132081	−1
p_4p_6	1	+0.000093989	−2
d_3d_4	2	+0.000084212	−3
p_6p_7	2	−0.000080242	−2
$(p_7)^2$		−0.000078225	−3
$(d_4)^2$		−0.000076230	−3
s_4s_6	2	−0.000069208	+1
d_3d_4	1	+0.000046353	−2
$(p_6)^2$		−0.000045181	−1

[a] See footnotes in Table VII.
[b] Classification is given in Table IV.
[c] See footnote e in Table VII.
[d] See footnote f in Table VII.

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[41] See, e.g., O. Sinanoglu, Adv. Chem. Phys. 6, 315 (1964), and references therein. A considerable amount of literature on the subject is currently being published.

TABLE X. Effect of (s_1) excitations.

Configuration[a]	Eigenvector[a]	Partial energies[a]
s_5	$+0.000435429$	-2[b]

[a] See footnotes in Table VII.
[b] See footnote f in Table VII.

electron-pair wave function,[42] like the one shown in Eq. (1), but without the strong orthogonality condition. We have

$$K(1,2)=(s_1)^2+[a_1(p_2)^2+a_2(s_4)^2+a_3(s_3s_4)+a_4(p_1p_2)+a_5(s_3)^2+a_6(d_2)^2+a_7(p_4)^2+\cdots]/c_0, \quad (4)$$

$$L(3,4)=c_0(s_2)^2+b_1(p_1)^2+b_2(s_3)^2+b_3(d_1)^2+b_4(p_3)^2+\cdots,$$

with $c_0=0.953115148$; the a_i and b_j coefficients are those of Tables VII and VIII, respectively. The third column of Table XIV shows this relationship. The total energy effect of quadruple excitations is -0.00352 a.u.

The first-order density matrix, as well as a plot of the electronic density, have not been included,[16] awaiting a better wave function. The electronic density decreases more sharply than the HF one at distances over 5.00 a.u.; the agreement with the HF density is 99.9% at the K-shell maximum, 101.5% at the L-shell maximum, 90% at 4.00 a.u., and 80% at 7.00 a.u. The second-order density matrix is being calculated and analyzed at the University of Florida by Smith and Olympia.

V. DISCUSSION

A. Analysis of Energy Results

In Table XV we compare the angular energy limits for Be^{++} obtained in Ref. 43 with those calculated from our present orbital basis, with and without orbital s_2. It is seen that in Be^{++}, f and g orbitals alone give an energy contribution of -0.00108 a.u.; higher orbitals improve the energy by another -0.00032 a.u. We assume that the effects of the L shell on $\epsilon(1s,1s)$ [which come largely from the $(2s)^2$ "sea", through an exclusion principle mechanism, see Tables VI and XV], and those produced by quadruple excitations, etc., have been accounted for in our calculated wave function, in which case, the errors we already have in Be^{++} are those we expect to find in $\epsilon(1s,1s)$. In support of the above assumption we notice that:

TABLE XI. Effect of (s_2) excitations.

Configuration[a]	Eigenvector[a]	Partial energies[a]
s_3	-0.039402746	0[b]
s_4	-0.010472965	0[b]
s_5	$+0.009705274$	0[b]
s_6	-0.004905873	0[b]
s_7	-0.001421291	-44[c]

[a] See footnotes in Table VII.
[b] See footnote e in Table VII.
[c] See footnote f in Table VII.

TABLE XII. Effect of $s_1(s_2)^2$ excitations.

Configuration[a]	Degenerate element[a]	Eigenvector[a]	Partial energies[a]
$s_3p_1p_2$	1	$+0.002533166$	-64[b]
$s_4p_1p_2$	1	-0.001313788	-31
$s_5p_1p_2$	1	$+0.000889808$	-5
$(p_1)^2d_1$		$+0.000878217$	-4
$s_3p_1p_4$	1	-0.000832788	-4
$s_5p_1p_4$	1	-0.000364376	-3
$s_5(p_1)^2$		$+0.000350146$	-2
$(p_1)^2d_2$		-0.000280244	-3

[a] See footnotes in Table IX.
[b] See footnote f in Table VII.

(i) The energy effect of the s_2 orbital is -0.001640 a.u. (Table XV).

(ii) $\epsilon(1s,1s)$ increases 0.001643 a.u. when going from Be^{++} to a K-shell CI Be wave function (Table VI), which shows that 99.8% of this energy difference is due to the exclusion principle.

(iii) When increasing the orbital basis to 9s orbitals, the exclusion effects are found to be -0.0000008 a.u. The breakdown of the angular energy contributions to $\epsilon(1s,1s)$ is given in Table XVI.

We have not carried out a similar analysis for the L shell. Since (i) our orbital basis is generously distributed around the L-shell region, (ii) $\epsilon(2s,2s)$ converges very fast in the present calculation, and (iii) our L-shell CI is slightly better than Nesbet's[38] (Table VI), we think that the error in our spd limit for $\epsilon(2s,2s)$ must be not greater than 0.0002 a.u. Ahlrichs and Kutzelnigg[44] have estimated the energy contributions of f and g orbitals to the L-shell correlation energy as -0.0003 and -0.0001 a.u., respectively.[45]

TABLE XIII. Effect of $(s_1)^2s_2$ excitations.

Configuration[a]	Eigenvector[a]	Partial energies[a]
$s_4(p_1)^2$	$+0.002205050$	-81[b]
$s_3(p_1)^2$	-0.001581543	-28
$s_3(p_2)^2$	$+0.001146214$	-30
$(s_3)^2s_4$	-0.000805817	-12
$s_3(s_4)^2$	$+0.000746339$	-14
$s_5(p_1)^2$	-0.000355494	$+2$
$s_4(p_2)^2$	$+0.000339073$	-3
$s_5(p_2)^2$	-0.000298742	-2
$s_3(d_2)^2$	$+0.000260163$	-4
$s_3(p_4)^2$	$+0.000243913$	-4

[a] See footnotes in Table VII.
[b] See footnote f in Table VII.

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[42] V. A. Fock, Dokl. Akad. Nauk SSSR, **73**, 735 (1950); A. C. Hurley, J. Lennard-Jones, and J. A. Pople, Proc. Roy. Soc. (London) **A220**, 446 (1953), and references from Ref. 20. See also E. Kapuy, Theoret. Chim. Acta **6**, 281 (1966).

[43] C. F. Bunge, paper II of this series, on He isoelectronic series (unpublished).

[44] R. Ahlrichs and W. Kutzelnigg, calculations contributed to the Density Matrix Conference, Queen's University, Kingston, Ontario 1967 (unpublished).

[45] These authors report partial energy contributions, which for high l orbitals are lower than the actual energy contributions, when using a single determinant as zeroth-order function (see Sec. V B).

TABLE XIV. Effect of quadruple excitations.

Configuration	Degenerate element	Eigenvector	a_ib_j/c_0[a,b]	Partial energies
$(p_1)^2(p_2)^2$	1	-0.008100156	-0.00877	0[c]
$(s_4)^2(p_1)^2$		$+0.005188415$	$+0.00517$	0[c]
$s_3s_4(p_1)^2$		-0.004387180	-0.00427	0[c]
$(p_1)^2(p_2)^2$	2	-0.002788241	$\cdots$[a]	-180[d]
$(p_1)^2(p_2)^2$	3	$+0.002304868$	$\cdots$[a]	-119
$(s_3)^2(p_1)^2$		$+0.002235701$	$+0.00199$	-55
$(p_1)^3p_2$		-0.002089968	-0.00261	-66
$(p_1)^2(d_2)^2$	1	$+0.001541815$	$+0.00196$	-136
$(p_1)^2(p_4)^2$	1	-0.001485312	-0.00157	-136
$(s_3)^2(p_2)^2$		$+0.001165107$	$+0.00118$	-33
$(p_1)^2(d_2)^2$	2	-0.001165085	$\cdots$[a]	-76
$(p_1)^4$		$+0.000586788$	$+0.00033$	-3
$(s_5)^2(p_1)^2$		$+0.000577759$	$+0.00055$	-18
$s_5s_6(p_1)^2$		$+0.000568549$	$+0.00055$	-26
$(p_1)^2(p_4)^2$	2	-0.000520967	$\cdots$[a]	-17
$(p_1)^2p_3p_4$	1	$+0.000500326$	$+0.00059$	-12
$(p_1)^2(p_5)^2$	1	-0.000481737	-0.00046	-23
$(p_1)^2(p_4)^2$	3	$+0.000428465$	$\cdots$[a]	-11
$(s_6)^2(p_1)^2$		$+0.000421847$	$+0.00042$	-17
$(p_2)^2(d_1)^2$	1	$+0.000408023$	$+0.00050$	-4
$(p_1)^2(d_3)^2$	1	$+0.000407066$	$+0.00054$[a]	-26
$(s_3)^2p_1p_2$		$+0.000379823$	$+0.00035$	-2
$s_4s_5(p_1)^2$		$+0.000347134$	$+0.00036$	-6
$(p_1)^3p_4$		$+0.000344052$	$+0.00051$	-3
$s_3s_5(p_1)^2$		$+0.000325242$	$+0.00028$	-2
$(s_4)^2(d_1)^2$		$+0.000320739$	$+0.00029$	-3
$(p_2)^2(d_1)^2$	2	-0.000308877	$\cdots$[a]	-2
$(p_1)^2(d_3)^2$	2	-0.000307497	$\cdots$[a]	-15
$(s_3)^2(d_2)^2$		$+0.000258591$	$+0.00026$	-4
$(p_1)^2(p_6)^2$	1	-0.000235096	-0.00017[a]	-5
$(s_3)^2(p_4)^2$		$+0.000229011$	$+0.00021$	-3
$s_3s_6(p_1)^2$		$+0.000201621$	$+0.00020$	-2
$(s_7)^2(p_1)^2$		$+0.000185323$	$+0.00018$	-2
$(p_1)^2(p_5)^2$	2	-0.000167933	$\cdots$[a]	-3
$s_6s_7(p_1)^2$		-0.000142831	-0.00010	-4
$(p_1)^2(d_4)^2$	1	$+0.000108959$	$+0.00010$	-5
$(p_1)^2(p_7)^2$	1	-0.000096088	-0.00009	-4
$(p_1)^2(d_4)^2$	2	-0.000082133	$\cdots$[a]	-3
$s_5s_7(p_1)^2$		$+0.000062347$	$+0.00006$	$+1$
$(p_1)^2p_2p_4$	2	-0.000036087	$\cdots$[a]	-1

[a] Phases are adjusted according to Tables III and IV. Since the K and L functions given by Eq. (4) are not normalized, the fourth column should be interpreted accordingly. When degenerate configurations occur, the various couplings should have been considered, but this has not been attempted here.

[b] Compare with O. Sinanoglu, J. Chem. Phys. 36, 706 (1962).

[c] See footnote e in Table VII.

[d] See footnote f in Table VII.

Regarding $\epsilon(1s,2s)$, our calculated value is within the 5% of error of Kelly's estimate, and it is probably correct (in an *spd* approximation) to within a few units in the fifth decimal. From BJ's calculation, it seems reasonable to estimate the corresponding energy contributions of f and higher orbitals to be less than -0.0001 a.u.[46]

From the previous considerations we get $E=-14.66453$ a.u. as a very likely upper bound to the *spd* energy limit, and $E=-14.66639$ a.u. is probably an upper bound to the exact nonrelativistic energy with an error not greater than 0.0003 a.u.

The energy estimates made in this section should serve to guide more accurate calculations, by regulating the emphasis to be spent on the exploration of each "portion" of a Be ground-state wave function. Also, we find a disagreement of 0.0009 a.u. with the previous estimate of the nonrelativistic energy (see Table V).In part, this may be due to using an HF wave function in the computation of the relativistic corrections.

B. Comparison with Recent Works

As pointed out in Sec. IV, it is difficult to compare our results, in a direct way, with those obtained by the application of Sinanoglu's theory. Sinanoglu assumes that single and triple excitations make negligible energy contributions when the HF orbitals are included in the one-electron basis. However, we get corresponding energy contributions of -0.00083 a.u. (about 1% of the correlation energy). Energy contributions of -0.000006 a.u. are found when instead of HF orbitals, the NO's of the final wave function are employed. Thus, we may conclude that in order to expect "small remainders" in accurate numerical applications of Sinanoglu's theory (i.e., where 0.001 a.u. are important), these should be carried out with a NO basis. For atomic states which are not "closed shell," the NO's themselves may not be symmetry adapted and thus our conjecture may turn out to be impractical.

The energy results of Byron and Joachain[39] are consistent with ours, if we assume that the errors (of the order of 0.001 a.u.) involved in their approximation to the third-order energy E_3 would have also lowered their value for $\epsilon(1s,1s)$. Their first-order correction φ_1 to the wave function, and their second-order correction φ_2, do not include single and triple excitations; we have seen that these, which affect both $\epsilon(1s,1s)$ and $\epsilon(2s,2s)$, lower the energy by about -0.00083 a.u. In this way we can rationalize the discrepancy of 0.00014 a.u. between BJ's value and our "exact" estimate [sixth- and further-order energies seem to make negligible contributions to $\epsilon(1s,1s)$; also, BJ's results on He, suggest that their radial expansions for each of the angular terms are the appropriate ones]. The error in $\epsilon(2s,2s)$, due to the slow convergence of the Rayleigh-Schrödinger (RS) perturbation theory for pairs of "outer" electrons, may well be smaller than -0.002 a.u. as pointed out by BJ, and it may also be subject to the same analysis as in the case of $\epsilon(1s,1s)$.

It is of interest to interpret the angular energy contributions to the individual pair energies in a RS perturbation framework. In a CI framework, we know that the right way of estimating this effect is to perform two CI calculations with and without a given set of angular contributions, and to take the difference between both energies; instead, the breakdown into p.e.'s[31] when employing an HF function as zeroth-order approximation, always gives underestimates for $l=0$ contributions, and overestimates for higher l values. The above considerations are probably valid also in the case of RS perturbation expansions, as may be seen by comparing the energy breakdown for E_2, E_3, E_4, and E_5 in terms of l contributions[39] with our values in Tables V and XVI. In this case, it is safe to assume that

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[46] See Sec. V B.

TABLE XV. Angular energy limits for Be^{++}.

	s	sp	spd	$spdf$	$spdfg$	E(total)
Weiss[a]	−13.62678	−13.65096	−13.65393	−13.65463	−13.65481	
Present orbital basis	−13.626709	−13.650908	−13.653825			
Same with s_2 excluded			−13.652185			
Reference 43 (calc.)	−13.626855	−13.651104	−13.654145			
"Exact" (Ref. 43)	−13.626858	−13.651116	−13.654169	−13.65497[b]	−13.65525[b]	−13.65557[c]
E_{HF}[d]	−13.611256					

[a] Reference 33.
[b] Upper bounds, estimated from rates of convergence of NO expansion (Ref. 43).
[c] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).
[d] E. Clementi, *Tables of Atomic Functions* (San Jose Research Laboratory, IBM Corporation, San Jose, Calif.)

the "real" energy contributions to $\epsilon(1s,2s)$ coming from f and higher orbitals are less than −0.0001 a.u.

Since the obtaining of the first-order correction φ_1 can be related to the minimization of E_2, it is of interest to see how this step affects E_2 and the rate of convergence of the energy in the RS expansion. Byron and Joachain include in φ_1 only doubly excited configurations, and they get, through third order in the energy, $E=-14.6585$ a.u. By doing a CI (HF+double excitations), we get $E=-14.6602$ a.u., and consequently an (upper) limiting value of −14.6624 a.u. (see Table XVI). Thus, a difference of −0.0039 a.u. results largely as a consequence of determining the expansion coefficients by a variational procedure rather than by RS perturbation theory, and in a smaller amount from the errors in E_3.

Nesbet's method has been clearly described[38]; in Table VI we compare his particular pair energies with the ones obtained in this work. The intershell pair energies arising in this case require the consideration of wave functions which are mixtures of singlet and triplet states, and thus we have not calculated them. Since we have included all significant configurations,[47] and in view of the estimated values for the "real" $\epsilon(1s,2s)$, it is likely that Nesbet's estimation of the correlation energy is not more than 0.0002 a.u. lower than the value he would have obtained by computing $E=\langle\Phi H\Phi\rangle/\langle\Phi\Phi\rangle$, which is well within his estimated margin of accuracy.

TABLE XVI. Estimates of total and pair energies.

	$\epsilon(1s,1s)$	$\epsilon(2s,2s)$	$\epsilon(1s,2s)$	E(total)
spd limit (this calc.)	−0.040869	−0.045104	−0.005240	−14.66419
Corrections for *spd* limit	−0.00034[a]	···	···	− 0.00034
Corrections for *f* and *g* orbitals	−0.00108[b]	−0.00040[c]	−0.00006[d]	− 0.00154
Corrections for higher orbitals	−0.00032[b]	?	···	− 0.00032
Final estimates	−0.04261[e]	−0.04550[e]	−0.00530[e]	−14.66639[f]

[a] Obtained by subtracting an "exact" from a calculated *spd*-energy limit (Table XV).
[b] See Table XV.
[c] See Refs. 44 and 45.
[d] See Refs. 39 and 46.
[e] Not necessarily upper bounds; probably with appreciable errors in the fifth decimal.
[f] Probably an upper bound with an error not greater than 0.0003 a.u.

Szasz and Byrne claim to have obtained energy limits for K- and L-shell CI (single excitations included). However, Nesbet's results and ours (Table VI) show that this is not the case; moreover, they report an energy $E=-14.6565$ a.u. for the corresponding "combination" CI: [(HF+$(1s)^2$ excitations+$(2s)^2$ excitations+single excitations]. We get instead an energy $E=-14.65604$ a.u. and a limiting value of −14.6582 a.u. (in an NO basis, the "combination" CI gives an energy of −14.6564 a.u.; no limiting value is given in this case). For the moment, we reserve our opinion on SB's discouraging result.[48]

C. Conclusions

In this paper we have developed a strategy which permits us to carry out conventional CI calculations accurate both in the energy and in the wave function. We have also shown, for the case of the ground state of Be, how the energy errors can be estimated within a CI framework without much effort; the estimated pair energies in Table XVI have probably an error of less than five units in the last figure. The importance of considering the full space of degenerate configurations shall not become evident before calculations for the ^3P, ^1D, and ^1S states of carbon are reported.[26]

The only shortcoming of the KL-shell NO basis seems to be its inadequacy to yield a fast convergent expansion for the intershell excitations ($1s2s$). To date, it is unknown how well a Hylleraas-type expansion can do in this case.

In further calculations, when searching for an orbital basis, we depart from the HF basis (but not from the HF space) and allow instead all possible double excitations to be included. The NO's of this pair CI are then taken as the basis for an unrestricted CI. A few double excitations are excluded by the requirements that (i) the "ground" NO's must expand the HF space, and (ii) the NO's must be symmetry adapted (e.g., no mixture of s and d orbitals is permitted). Except for ^1S states, we shall not be dealing with NO's but with orthonormal

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[47] Upon revision of our results, we have noticed that the configuration $(s_3)^2(s_4)^2$, which should occur with eigenvector component +0.0060 and partial energy −0.000012 a.u., was inadvertently left out from the final configuration search.

[48] Szasz and Byrne's calculation is being repeated and extended here at Indiana University, by J. S. Sims, using analytic integration techniques.

symmetry-adapted orbitals, whose radial parts are those of some natural spin orbitals with given m_l and m_s quantum numbers; these questions will be elaborated elsewhere.[26]

We shall conclude by attempting to give an optimistic view for the future of conventional CI calculations of high accuracy. The very fact that 1492 Slater determinants were employed in this calculation may be for many a first class argument to maintain that this type of approach is not very convenient. In addition, the number of Slater determinants cannot be considerably reduced by a better choice of the STO basis, as can be demonstrated by expressing the final wave function in a NO basis (WF2, Sec. IV). We must then notice that:

(i) The number that counts is the number of configurations, which is 180; of these only 91 are instrumental in lowering the energy within 0.0005 a.u. of the final result; however, some of the remaining configurations may affect properties other than the energy.

(ii) CI is a general method for any symmetry and for excited states.

(iii) CI is "exact", as far as numerical errors are kept within bounds.

We cannot discuss objectively whether this approach requires more or less effort than others; computational times are reported in Secs. I and III. The organization of the work is simple, which is probably true of other methods as well. The discussion in this section should suffice to persuade that at the present time, the calculation of highly accurate atomic wave functions is not a "one-man, one-method show," but requires the bringing together of many methods, each with its particular advantages and limitations,

Certainly, we are going to see in the future a good amount of work along the lines presented here. We are currently working on several states of first-row atoms up to Ne.

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