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Multireferent superposition-of-configurations calculations of core-correlation effects on energy levels and oscillator strengths: Be and B^+

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The superposition-of-configurations (SOC) method is used to calculate intershell and core-correlation corrections to energy levels for the low-lying states of Be and B^+ belonging to the configurations $2s^2$, $2s2p$, and $2p^2$ and the singlets of $2s3s$ and $2s3d$. The wave functions are also used to calculate the oscillator strengths for all allowed transitions among these states. Transition energies are calculated with an accuracy ranging from 10 to 50 cm^{-1} and the oscillator strengths are estimated to be accurate to 1–2 %. The SOC wave functions are single- and double-substitution calculations based on a multiconfiguration referent, where the reference set is derived from a two-electron natural-orbital transformation of valence-shell-correlated SOC functions. It is found that a fairly substantial reference set is necessary to obtain these results, ranging from three configuration-state functions (CSFs) for $2s2p\ {}^3P$ and $2p^2\ {}^3P$ to 11 CSFs for $2s3s\ {}^1S$. Intershell correlations are necessary for both energy differences and oscillator strengths, but core correlations with angular symmetries higher than $l=1$ (p orbitals) are not.

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INTRODUCTION

It is common in atomic structure calculations to neglect correlation corrections arising from the core electrons or to include them in only a minimal fashion. This amounts to assuming that such core-related correlation energy corrections remain approximately unchanged by excitation or even removal of a valence electron, so that in calculating energy differences these corrections very nearly cancel out, even though the total correlation energy associated with the core is quite substantial. With regard to the calculation of multiplet strengths of a dipole transition, neglecting core effects is usually justified by the fact that the dipole operator skews the multielectron integrand of the transition moment to the outer, i.e., the valence, region of the atom. This is less valid for the velocity form of the matrix element, which is the basis for the preference usually given the length form.

These errors are in fact rather small, so that neglecting core and core-valence correlation is usually a pretty good approximation. As long as the correlations are smaller than or of the same order as the errors in the valence-shell-correlation calculations, there is little point to increasing the complexity of the computational problem so as to fully account for core effects. However, *ab initio* spectroscopic calculations on the lighter elements which are reasonably complete in their treatment of correlation are now becoming routine, producing an increasing body of useful atomic data [1]. While there is little doubt that such data are quite reliable, it is important to explore systematically the limits imposed by these core-correlation effects.

This paper therefore reports the results of extensive calculations of core- and core-valence-correlation effects on the ground state and a variety of excited states of the beryllium atom and the isoelectronic singly ionized boron atom. In particular, calculations have been done for the energies of $2s^2\ {}^1S$, $2s2p\ {}^{1,3}P$, $2p^2\ {}^3P$, ${}^1D$, and ${}^1S$ (B^+ only) and the singlet states of $2s3s$ and $2s3d$, as well as the oscillator strengths for all dipole-allowed transitions among them. The method of calculation adopted is the superposition-of-configurations (SOC) approach, based on variational analytic Slater-type orbitals (STOs), with configuration-state functions (CSFs) defined by single and double (SD) substitutions into some set of reference CSFs.

Since valence-shell correlation for these four-electron systems frequently involves strong configuration interaction, the problem also lends itself readily to a study of the multiconfiguration referent correlation problem as well, and particular attention will be given to the dependence of the results on the reference set, i.e., the set of valence-shell configurations with respect to which the single and double substitution configurations are defined. This aspect of the correlation problem for the beryllium atom has recently been discussed extensively from the standpoint of many-body perturbation theory [2].

The classic work on the ground-state correlation energy of beryllium is the extensive configuration-interaction (CI) calculation of Bunge [3]. Within the past few years, there have appeared a large number of very accurate calculations based on perturbative methods [4] as well as CI [5], some of which have also included isoelectronic positive ions [6,7]. All these calculations are directed toward an accurate calculation of the total energy of the atom and most of them pertain only to the ground state.

The main concern here will be to identify and evaluate those elements of the correlation calculation which are necessary for the accurate determination of energy differences and transition oscillator strengths and those which are not. Thus, while the calculations are directed toward minimizing the total energy of each state, the

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most accurate possible total energy is not the primary goal. Indeed, we will find that a large part of the total correlation is quite irrelevant for theoretical spectroscopy of the valence shell. To this end, the contributions of core-valence, i.e., intershell, correlation and core correlation will be evaluated sequentially. Convergence of both components with respect to angular correlation will also be examined, as will the effects of choosing a minimal reference set versus a more complete one. In each case, the emphasis will be on the transition energies and transition oscillator strengths.

The next section will describe, in detail, the computational strategy adopted for this study. This will be followed by a description and evaluation of the results for both the total and ionization energies, followed in turn by a parallel evaluation of the results for oscillator strengths. With regard to the latter, since the calculations also include extensive treatment of the core- and intershell-correlation corrections, considerable weight will be given to the agreement of the length and velocity forms of the oscillator strengths.

These calculations realize an accuracy for the ionization energies of the low-lying states of Be and B^+ in the range 10–50 cm^{-1}. To achieve this, an exhaustive treatment of intershell correlation is necessary. An exhaustive treatment of core correlation is not. It is important for the core-correlation configurations through *s* and *p* symmetries ($l=0,1$) to be fairly complete, since they give rise to differential energy shifts ranging from -150 to $+90$ cm^{-1}, depending on the state and the ion. However, all the higher angular terms, which are so important in the slow convergence of *K*-shell correlation energies, contribute virtually nothing, no more than 1–2 cm^{-1}, to the excitation and ionization energies. The computed ionization energy of the $2s3s\,{}^1S$ state of B^+ disagrees with experiment by 680 cm^{-1}, in spite of special efforts to include all relevant correlations.

As for the oscillator strengths, the largest length-velocity (*l*-*v*) discrepancy turns out to be about 2%, with the *l*-*v* agreement usually being better than 1%. Here too the higher angular momentum core correlations are of no consequence. There are no significant discrepancies with available experimental data, within the stated experimental uncertainties. It is necessary to go beyond the minimal reference set to achieve the accuracies just quoted, more so for the energy differences than oscillator strengths.

COMPUTATIONAL STRATEGY

For a berylliumlike atom, the multi-referent SOC trial function used here has the general form

$$\begin{aligned}\Phi=&\sum_{a,b} c_{ab}\,1s^2\varphi_a\varphi_b+\sum_{i,j} c_{ij}\,1s^2\varphi_i\varphi_j\\&+\sum_{a,b}\sum_{i,j}\{c_{a,ij}\,1s\varphi_a\varphi_i\varphi_j+c_{b,ij}\,1s\varphi_b\varphi_i\varphi_j\}\\&+\sum_{a,b}\sum_{i,j}c_{ab,ij}\varphi_a\varphi_b(\varphi_i\varphi_j\,{}^1S)\ . \qquad (1)\end{aligned}$$

The first sum here runs over the reference set of CSFs and the second represents the remainder of the valence-shell correlation. The next two sums, in which one 1*s* orbital and one of the referent orbitals remain occupied, correspond to intershell, or core-valence, correlation within the context of a multiconfiguration referent. Finally, the last sum, with both 1*s* electrons replaced by correlation orbitals, represents the core correlation. In all cases both orbital and spin angular momenta are coupled to be eigenfunctions of $\mathcal{L}^2$ and S^2 so that each term in Eq. (1) is a fully symmetry-adapted configuration-state function. The variational principle, of course, requires the expansion coefficients to be the elements of an eigenvector of the Hamiltonian matrix, over whatever basis CSFs have been included in Eq. (1).

In all the core-correlation configurations, the $1s^2$ replacement pair is always coupled to be ${}^1S$ only, even though others may be possible. In fact, except for the $2s^2\,{}^1S$ ground state, the core double-substitution configurations can be coupled in a number of different ways. Furthermore, for the intershell terms, only those CSFs are included in which the double-substitution pair is coupled consistently with the two-particle fractional parentage of the referent. Thus, e.g., if the reference CSF is $1s^22p^2\,{}^1D$, a typical intershell configuration might have the form $1s2p3d4f$, in which case the couplings

$$(1s2p\ {}^1P)(3d4f\ {}^1P),\quad (1s2p\ {}^3P)(3d4f\ {}^3P)$$

would be allowed. However,

$$(1s2p\,{}^1P)(3d4f\,{}^1D),\quad (1s2p\,{}^1P)(3d4f\,{}^1F)\ ,$$
$$(1s2p\,{}^3P)(3d4f\,{}^3D),\quad (1s2p\,{}^3P)(3d4f\,{}^3F)$$

would not, since the substitution pairs are not coupled the same as the $1s2p$ pair being replaced, i.e., either ${}^1P$ or ${}^3P$.

This restriction to "parent-coupled" configurations considerably diminishes, by as smuch as a factor of about 3, the total number of CSFs in the SOC wave function had all possible couplings been included. It should not, however, represent a significant constraint on the physics of the problem, since the excluded terms do not interact directly with the referent CSF. This will be borne out later by a few sample calulations of minimal referent wave functions.

The orbitals used in the SOC function (1) are represented by an expansion in terms of analytic basis functions

$$\varphi_{nlm}(r,\theta,\phi)=\sum_i c_{nli}\chi_{il}(\zeta_i,r)Y_l^m(\theta,\phi)\ , \qquad (2)$$

which are the normalized Slater-type orbitals

$$\chi_{il}=N_i r^{p_i-1}e^{-\zeta_i r}\ . \qquad (3)$$

The first stage in determining a basis set was to perform a set of expansion method Hartree-Fock (HF) calculations for the most likely dominant configuration. Whether or not it is in fact dominant is not really of much importance, since the main purpose of the HF calculations is only to determine a 1*s* core orbital, which is not very sensitive to the *L*-shell correlation. The correlation basis set for each state actually consists of two groups of functions, one chosen to correlate the *K* shell and one chosen to correlate the valence, or valence Rydberg, shell.

For the valence-shell-correlation problem, each state was treated entirely independently of every other state, even those of the same symmetry. Hartree-Fock orbitals were used in the initial round of calculations to determine the 1*s* orbital for each state. Further basis functions were added and the total energy minimized with respect to their free parameters for SOC trial functions including all possible valence correlation CSFs which could be constructed from the basis. In the case of second or third excited states of the same symmetry, the entire variational effort was concentrated on the appropriate eigenvalue of the matrix diagonalization problem. The cutoff for terminating this search was generally of the order of 10^{-5} a.u. in the total energy.

After some numerical experimentation, a double ζ type of STO basis was usually, but not always, settled on for all but the higher symmetries, i.e., $l=5,6$. This appeared generally to embody the best compromise between accuracy and difficulties of linear dependence. Within each ζ, the Slater "principal quantum number" p_i was allowed to run from $p_i=l+1$ to some maximum. For the ground state, a valence-shell basis set $\{5s,5p,4d,3f,2g,2h,1i\}$ was used with similar, but somewhat different, sets employed for each of the excited states; e.g., the $2p^2\,{}^1S$ state of B^+ required a $\{5s,5p,5d,4f,4g,4h,3i\}$ basis. All valence-shell basis sets included functions with symmetry through $l=6$ (*i* orbitals).

With these basis sets established, a two-electron natural-orbital transformation [8] was carried out on the final valence-shell SOC wave functions. For a two-electron singlet, for example, a SOC wave function has the general form

$$\Psi=\sum_i c_{ii}\phi_i(1)\phi_i(2)+\sum_{i<j}\frac{c_{ij}}{\sqrt{2}}\{\phi_i(1)\phi_j(2)+\phi_j(1)\phi_i(2)\}\ . \tag{4}$$

Diagonalizing the matrix of coefficients c_{ij} transforms the orbitals unitarily among themselves so that the wave function assumes a quadratic form

$$\Psi=\sum_i a_i\varphi_i(1)\varphi_i(2)\ , \tag{5}$$

where the φ_i are called the natural orbitals of the system. They are the most "rapidly convergent" in the sense that each succeeding term in Eq. (5) is the largest possible for the given basis [9]. Similar considerations apply also to triplets and to states where the orbitals are of different symmetry such as, e.g., $2s2p$. The value of this transformation is that it "concentrates" the correlation effectiveness of the orbitals into the first few of a rapidly converging sequence of orbitals, providing a natural set for the multireferent calculation of core and core-valence correlation. The two-electron natural-orbital transformation is approximately equivalent to a limited multiconfiguration Hartree-Fock (MCHF) calculation and it is exactly equivalent to a MCHF calculation that includes the full set of CSFs that can be constructed from the analytical basis.

The *K*-shell correlation basis set was the same for all states of each atom and was determined by variationally optimizing a SOC wave function for the ground state of the two-electron heliumlike ions Be^{2+} and B^{3+}. These calculations yielded a $\{3s,5p,5d,4f,4g,3h,2i\}$ set of fully optimized STOs, which captured better than 99% of the He-like ground-state correlation energy. The occurrence of only three *s*-type functions in this set is due to the fact that the calculations also made use of the *s* basis from the expansion method representation of the Hartree-Fock 1*s* function, which required three STOs. Here too the optimum set of STOs turned out to be a double ζ basis and these basis sets are given in the Appendix. Once the basis was determined, the SOC calculations were followed by a natural-orbital transformation to produce a set of *K*-shell correlation orbitals with optimum correlation convergence.

The merging of these two basis sets produced the final correlation basis for the full four-electron multireferent calculations. This was accomplished by appending the *K*-shell natural orbitals to the valence ones and then sequentially Schmidt orthogonalizing the entire set. Occasionally the last natural orbital from one or both sets was omitted, in order to minimize problems arising from linear dependence. For the valence-correlation part of the wave function, i.e., the second term of (1), the summations were taken over only the valence orbitals. However, for the intershell and *K*-shell correlation terms, the summations were made to run over the entire combined set of orbitals. The assumption here is that intershell correlation can be adequately represented by correlation orbitals obtained independently from the core and valence shells. This was verified by spot-check calculations on the ground state of beryllium by adding and optimizing basis functions to calculations which included only valence and intershell terms, but not core correlation, the latter being omitted to avoid possible distortions due to changes in the relatively large core correlation. The effect of such intershell augmentation was found to be entirely negligible and it was not pursued systematically for the other states.

RESULTS: ENERGY LEVELS

Two sets of valence-shell reference configurations were employed in this study and are listed in Table I. Set B is a minimal reference set in that it really makes little sense to attempt a SD SOC calculation based on anything less. Set A was adopted using the general rule that the reference set should comprise over 99% of the valence-correlation wave function, which as it happens is virtually the same composition as in the full SOC calculation. This means that, for the reference CSFs of Eq. (1),

$$\sum c_{ab}^2\geq 0.99\ .$$

Sometimes the reference set was enlarged beyond that called for by this criterion. For example, when a larger set was indicated for Be than for B^+, the largest set was used for both systems. Also, the $2s3s$ configuration was included in the ground-state calculations as a precaution against any tendency of the calculation to rotate the *s* basis when fully correlated, i.e., the total wave function is

TABLE I. Configuration-state functions included in the multiconfiguration reference sets for each of the states of Be and B^+ and their ionization limits calculated here. Totals are the maximum number of CSFs produced by single and double substitutions into the reference set.

No.	$2s^2\,{}^1S$	$2s2p\,{}^1P$	$2p^2\,{}^1D$	$2p^2\,{}^1S$	$2s3s\,{}^1S$	$2s3d\,{}^1D$	$2s2p\,{}^3P$	$2p^2\,{}^3P$	$1s^22s$
				Reference set A					
1	$2s^2$	$2s2p$	$2p^2$	$2s^2$	$2s^2$	$2p^2$	$2s2p$	$2p^2$	$1s^22s$
2	$2s3s$	$3s3p$	$3p^2$	$2s3s$	$2s3s$	$3p^2$	$3s3p$	$3p^2$	
3	$3s^2$	$2p3d$	$3d^2$	$3s^2$	$3s^2$	$3d^2$	$2p3d$	$3d^2$	
4	$2p^2$	$3p3d$	$3d4d$	$2p^2$	$4s^2$	$3d4d$			
5		$3d4f$	$4d^2$	$3p^2$	$2p^2$	$4d^2$			
6			$2s3d$	$3d^2$	$2p3p$	$2s3d$			
7			$2p4f$	$4f^2$	$3p^2$	$2p4f$			
8					$4p^2$				
9					$3d^2$				
10					$4d^2$				
11					$4f^2$				
Total number of CSFs generated	1995	5986	6240	4689	5570	6213	4698	3038	454
				Reference set B					
1	$2s^2$	$2s2p$	$2p^2$	$2s^2$	$2s^2$	$2p^2$	$2s2p$	$2p^2$	$1s^22s$
2	$2p^2$	$2p3d$	$2s3d$	$3s^2$	$2s3s$	$2s3d$			
3				$2p^2$	$3s^2$				
4					$2p^2$				
Total number of CSFs generated	1342	3272	2692	2329	2242	2680	1621	1060	454

invariant under any unitary transformation of the 2*s* and 3*s* orbitals.

At this point, it is of some interest to digress briefly to consider an important effect of correlation on the orbitals themselves. The 2*s*2*p* configuration of neutral beryllium is the archetype of strong orbital term dependence. It has been long known that the Hartree-Fock 2*p* orbital is distinctly different for the ${}^3P$ and ${}^1P$ states, the singlet orbital being much more diffuse than the triplet. Figure 1 shows the 2*p* Hartree-Fock radial functions for these states along with the natural orbital 2*p* function of the valence-shell SOC calculation, the latter being essentially the same as a multiconfiguration self-consistent field orbital. The "correlation relaxation" induced by the multiconfiguration environment has produced a much less term dependent 2*p* orbital, moving it substantially closer to that of the ${}^3P$ term, which, as it turns out, is virtually unchanged by correlation. The important point here is that the 2*s*2*p* configuration with this 2*p* function is the appropriate reference configuration for a full scale correlation calculation, not the Hartree-Fock configuration. One could, of course, use the Hartree-Fock configuration in a SOC calculation, but the reference set would then have to be enlarged so as to simulate this orbital relaxation.

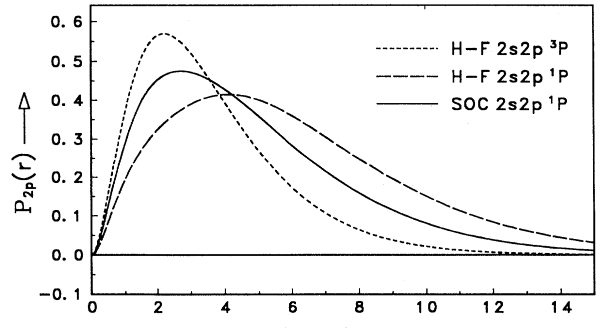

FIG. 1. Comparison of 2*p* radial functions for the 2*s*2*p* configuration of Be. HF refers to the Hartree-Fock approximation and SOC is the valence-shell natural orbital.

The total energies and ionization energies obtained with SOC calculations based on the optimal reference set, set A, are shown in Table II, for Be, and Table III, for B^+, and compared with the experimental ionization energies [10,11]. Also shown in these tables are the results of the corresponding calculations on the lithiumlike ion limit, which used the identical *K*-shell basis set, but independently determined intershell orbitals. Ionization energies are computed relative to the lithiumlike ion at exactly the same level of approximation. Entries labeled $L(l)$ are results obtained with only valence-shell configurations, but including all configurations with orbitals of symmetry through *l*. Those labeled $L+KL(l)$ are obtained from calculations that include all the valence CSFs plus the intershell configurations with orbitals of symmetry through *l*. Finally, the *K*-shell results refer to calculations with the full valence and intershell sets to which the core correlation configurations of the indicated symmetry have been added.

Since for some of the states the valence-correlation calculations have not fully converged with respect to the *l* series, this part of the correlation energy has been extrapolated, assuming an incremental correlation energy behaving as l^{-4} along the series. This is the correction labeled "l extrapolation" in the tables. No extrapolations were carried out for either the K-shell- or intershell-correlation energy contributions. Relativistic corrections were calculated for the reference set of configuration-interaction wave functions using the lowest-order Pauli operators, the standard Darwin and mass correction terms. Spin orbit, since it produces no shifts of the energy levels, was not included in these corrections. These are very light atoms and one would expect relativistic effects to be small, especially for the energy differences, as is indeed the case. For a precision better than 5–10 cm^{-1}, it may be desirable to do something more sophisticated, such as differencing the comparable nonrelativistic and Dirac-Fock calculations. However, there are some ambiguities here in determining exactly what is "comparable" in a multiconfiguration environment and in avoiding spurious nonrelativistic offsets [12].

The Davidson correction [13] is an attempt to estimate residual correlation shifts due to the neglect of triple- and quadruple-substitution configurations, based on the "unlinked" term in the fourth-order perturbation energy formula which is canceled by these configurations,

$$\delta E^{(4)} = E^{(2)} \langle \Psi^{(1)} | \Psi^{(1)} \rangle \ .$$

The Davidson formula adopted here is

$$\delta E = \Delta E \left[\frac{1 - \langle \Phi_{\text{ref}} | \Phi \rangle^2}{\langle \Phi_{\text{ref}} | \Phi \rangle^2} \right] \frac{(N-2)}{N} \ , \tag{6}$$

where ΔE is the computed total correlation energy and the scalar product is taken between the reference set wave function and the full SOC function. The latter product is simply the sum of the products of coefficients of the reference CSFs in the two functions. This formula was originally intended to estimate the magnitude of the unlinked terms in the fourth-order perturbation energy expression, based on a single-configuration zeroth-order referent. To a large extent these effects have already been included by basing the calculations on a multiconfiguration referent. There has been considerable discussion of the proper way to extend this correction to the multiconfiguration reference problem [14] and Eq. (6) is probably not an unreasonable version of such an extension. The last factor represents an *ad hoc* way of avoiding the counting of nonexistent unlinked contributions [15], N being the total number of electrons in the atom.

Several observations should be made about these results. First, for an accuracy in range of 50–100 cm^{-1}, intershell correlations are necessary for the prediction of

TABLE II. Total energies (in a.u.) and ionization energies (in 10^3 cm^{-1}) for Be, computed at various levels of approximation, based on the maximum CSF reference set, set A.

Approximation	$2s^2\,{}^1S$	$2s2p\,{}^1P$	$2p^2\,{}^1D$	$2s3s\,{}^1S$	$2s3d\,{}^1D$	$2s2p\,{}^3P$	$2p^2\,{}^3P$	$1s^22s$
				Total energy				
Referent CI	−14.618 39	−14.422 30	−14.359 35	−14.370 78	−14.325 41	−14.517 95	−14.345 11	−14.277 39
L (though d)	−14.619 04	−14.423 79	−14.359 81	−14.370 80	−14.325 89	−14.518 50	−14.345 36	
L (through g)	−14.619 20	−14.424 31	−14.359 98	−14.370 81	−14.326 02	−14.518 69	−14.345 69	
L (through h)	−14.619 22	−14.424 40	−14.360 00	−14.370 81	−14.326 03	−14.518 70	−14.345 70	
L (through i)	−14.619 22	−14.424 44	−14.360 00	−14.370 82	−14.326 04	−14.518 70	−14.345 71	
$L+KL$ (through d)	−14.624 24	−14.429 96	−14.364 30	−14.375 07	−14.330 37	−14.523 80	−14.351 16	−14.281 59
$L+KL$ (through g)	−14.624 34	−14.430 14	−14.364 56	−14.375 13	−14.330 49	−14.524 02	−14.351 50	−14.281 66
$L+KL$ (through i)	−14.624 35	−14.430 15	−14.364 57	−14.375 14	−14.330 49	−14.524 03	−14.351 51	−14.281 66
$L+KL+K$ (through p)	−14.662 67	−14.468 69	−14.403 59	−14.413 64	−14.369 13	−14.562 59	−14.390 79	−14.320 20
$L+KL+K$ (through h)	−14.666 89	−14.472 88	−14.407 78	−14.417 84	−14.373 32	−14.566 79	−14.394 98	−14.324 40
Relativistic	−14.669 45	−14.475 34	−14.410 20	−14.420 33	−14.375 79	−14.569 25	−14.397 37	−14.326 88
l extrapolation	−14.669 45	−14.475 39	−14.410 20	−14.420 34	−14.375 80	−14.569 26	−14.397 38	−14.326 88
Davidson correction	−14.669 51	−14.475 50	−14.410 27	−14.420 39	−14.376 08	−14.569 33	−14.397 45	−14.326 91
				Ionization energy				
Referent CI	−74.837	−31.802	−17.987	−20.496	−10.538	−52.794	−14.862	
L (through d)	−74.979	−32.129	−18.088	−20.501	−10.643	−52.916	−14.918	
L (through g)	−75.015	−32.244	−18.126	−20.503	−10.672	−52.957	−14.990	
L (through h)	−75.018	−32.264	−18.129	−20.503	−10.675	−52.958	−14.992	
L (through i)	−75.020	−32.272	−18.130	−20.503	−10.676	−52.959	−14.993	
$L+KL$ (through d)	−75.199	−32.561	−18.152	−20.515	−10.706	−53.155	−15.269	
$L+KL$ (through g)	−75.207	−32.586	−18.195	−20.515	−10.717	−53.189	−15.327	
$L+KL$ (through i)	−75.207	−32.587	−18.196	−20.514	−10.717	−53.190	−15.329	
$L+KL+K$ (through p)	−75.159	−32.587	−18.301	−20.506	−10.739	−53.196	−15.491	
$L+KL+K$ (through h)	−75.163	−32.585	−18.299	−20.506	−10.736	−53.195	−15.489	
Relativistic	−75.180	−32.580	−18.286	−20.509	−10.734	−53.191	−15.469	
l extrapolation	−75.180	−32.591	−18.286	−20.511	−10.737	−53.193	−15.471	
Davidson correction	−75.187	−32.608	−18.294	−20.515	−10.789	−53.202	−15.481	
Experiment[a]	−75.192	−32.627	−18.310	−20.515	−10.764	−53.212	−15.497	

[a] See Ref. [10].

the ionization energies. Second, core correlations through $l=1$ are also necessary, although their effect is generally opposite that of the intershell correlation. Intershell corrections always drive the energy down relative to the ion limit. Core-correlation corrections, while pushing the total energy down by a large amount, are usually not as effective as in the lithiumlike ion and therefore the ionization energy is raised somewhat and by differing amounts depending on whether the $2s$ in the major referent is fully occupied, half occupied, or unoccupied, as well as on the occupancy of the $2p$ orbital [16,17]. This means that the K-shell-correlation energy is different for each of the states treated here and is different from the correlation energy of heliumlike beryllium. The K-shell energy correction for the Be ground state is computed here to be $-0.042\,54$ a.u., whereas the comparable calculation for heliumlike Be^{2+} gives $-0.044\,01$ a.u. All of the remaining contributions of the harmonic series to the core-correlation energy, however, are, to within 1 cm^{-1}, identical for all states considered here as well as the ion limit for both Be and B^+. This core-correlation series, of course, is responsible for the slow convergence of the total correlation energy, but is totally irrelevant for the determination of excitation energies. The "exact nonrelativistic" total energy for the ground state of Be is $-14.667\,36$ a.u. [3,6] and for B^+ it is $-23.348\,92$ a.u. [6]. The errors in the energies computed here of 0.00037 and 0.00055 a.u., respectively, can be mostly accounted for by truncations in the K-shell-correlation calculation.

In view of the fact that the ground state of the beryllium atom has been for so long a favorite target for theoretical calculations, it is appropriate to make some comparison with the most recent total-energy results; this is done in Table IV. The best estimates of the exact nonrelativistic total energy indicate that the current results are in error by about 90 cm^{-1}. All the directly calculated results, however, agree considerably better with each other and with the results of this paper, especially considering the fact that for all the other CI calculations, the K-shell correlation is truncated at i orbitals. For the present calculation, the K-shell correlation is truncated at h orbitals ($l=5$) and no attempt has been made to extrapolate this correction. The estimated exact values have been obtained by combining the l-extrapolated total correlation energy with estimates of the basis set truncation errors.

While the ground state, except for the K shell, seems to have converged rather well, it is somewhat disconcerting that, even for the valence correlation, not all of the states have converged even though valence-shell CSFs through

TABLE III. Total energies (in a.u.) and ionization energies (in 10^3 cm^{-1}) for B^+, computed at various levels of approximation, based on the maximum CSF reference set, set A.

Approximation	$2s^2\,{}^1S$	$2s2p\,{}^1P$	$2p^2\,{}^1D$	$2p^2\,{}^1S$	$2s3s\,{}^1S$	$2s3d\,{}^1D$	$2s2p\,{}^3P$	$2p^2\,{}^3P$	$1s^22s$
				Total energy					
Referent CI	−24.297 79	−23.958 14	−23.828 55	−23.712 87	−23.670 58	−23.593 73	−24.127 08	−23.843 84	−23.375 97
L (through d)	−24.298 78	−23.960 29	−23.829 37	−23.712 87	−23.670 86	−23.594 29	−24.127 46	−23.844 18	
L (through g)	−24.299 05	−23.961 31	−23.830 11	−23.715 44	−23.671 32	−23.595 06	−24.127 74	−23.844 64	
L (through h)	−24.299 07	−23.961 52	−23.830 20	−23.715 66	−23.671 44	−23.595 13	−24.127 75	−23.844 66	
L (through i)	−24.299 08	−23.961 61	−23.830 23	−23.715 75	−23.671 49	−23.595 15	−24.127 75	−23.844 66	
$L+KL$ (through d)	−24.305 70	−23.970 82	−23.838 06	−23.722 90	−23.678 19	−23.600 66	−24.135 27	−23.853 83	−23.381 22
$L+KL$ (through g)	−24.305 85	−23.971 22	−23.838 70	−23.723 41	−23.678 39	−23.600 79	−24.135 67	−23.854 46	−23.381 31
$L+KL$ (through i)	−24.305 86	−23.971 24	−23.838 74	−23.723 45	−23.678 41	−23.600 80	−24.135 69	−23.854 49	−23.381 32
$L+KL+K$ (through p)	−24.343 89	−24.009 52	−23.877 84	−23.762 37	−23.716 98	−23.639 26	−24.173 98	−23.893 62	−23.419 78
$L+KL+K$ (through h)	−24.348 37	−24.013 97	−23.882 30	−23.766 83	−23.721 43	−23.643 70	−24.178 44	−23.898 07	−23.424 23
Relativistic	−24.355 20	−24.020 57	−23.888 64	−23.773 27	−23.727 94	−23.650 27	−24.185 05	−23.904 40	−23.430 81
l extrapolation	−24.355 21	−24.020 68	−23.888 67	−23.773 38	−23.728 00	−23.650 30	−24.185 06	−23.904 41	−23.430 81
Davidson correction	−24.355 25	−24.020 77	−23.888 73	−23.773 59	−23.728 21	−23.650 37	−24.185 11	−23.904 47	−23.430 83
				Ionization energy					
Referent CI	−202.307	−127.765	−99.325	−73.937	−64.657	−47.790	−164.842	−102.681	
L (through d)	−202.523	−128.237	−99.505	−73.937	−64.718	−47.914	−164.926	−102.755	
L (through g)	−202.582	−128.462	−99.667	−74.501	−64.819	−48.082	−164.986	−102.856	
L (through h)	−202.588	−128.507	−99.688	−74.549	−64.845	−48.099	−164.988	−102.860	
L (through i)	−202.590	−128.526	−99.694	−74.570	−64.856	−48.103	−164.988	−102.861	
$L+KL$ (through d)	−202.890	−129.395	−100.259	−74.986	−65.174	−48.160	−165.486	−103.721	
$L+KL$ (through g)	−202.904	−129.463	−100.381	−75.079	−65.198	−48.168	−165.555	−103.839	
$L+KL$ (through i)	−202.904	−129.467	−100.388	−75.085	−65.200	−48.168	−165.558	−103.845	
$L+KL+K$ (through p)	−202.810	−129.427	−100.528	−75.187	−65.224	−48.168	−165.520	−103.990	
$L+KL+K$ (through h)	−202.815	−129.426	−100.530	−75.188	−65.223	−48.166	−165.521	−103.991	
Relativistic	−202.870	−129.431	−100.477	−75.157	−65.208	−48.162	−165.529	−103.936	
l extrapolation	−202.872	−129.455	−100.484	−75.181	−65.221	−48.169	−165.531	−103.938	
Davidson correction	−202.877	−129.469	−100.492	−75.223	−65.265	−48.180	−165.536	−103.946	
Experiment[a]	−202.887	−129.491	−100.524	−75.226	−65.909[b]	−48.201	−165.537	−103.960	

[a] See Ref. [11].

[b] See Ref. [19].

TABLE IV. Comparison with other theoretical results for the total energy (in a.u.) of the ground state of neutral beryllium.

Reference	Total energy (a.u.) Direct calculated	Estimated exact
Bunge [3], CI	−14.666 90	−14.667 33
Rizzo, Clementi, and Sekiya [5], CI	−14.666 96	
Chung, Zhu, and Wang [7], CI	−14.667 04	−14.667 35
Davidson *et al.* [6], CI	−14.667 18	−14.667 36
This work	−14.666 89	

$l=6$ were included. This problem gets worse for higher Z, as indicated by the B^+ results where, for the $2s2p\ ^1P$ and $2p^2\ ^1S$ states, adding CSFs containing i orbitals results in an energy correction of 20 cm^{-1}. The Davidson correction normally results in a small improvement in the binding-energy prediction and the largest difference between calculated and experimental ionization energies, with one exception, is 30 cm^{-1} for the lowest ^1D state in B^+.

This exception, however, is particularly perplexing. The $2s3s\ ^1S$ term in B^+ still disagrees from experiment by 640 cm^{-1}, while for Be it is calculated almost exactly. In fact, the initial indication of this discrepancy prompted the inclusion of more configurations in the reference set than for any other state. It is possible that the problem is related to this state being the third eigenvalue for B^+, while it is only the second in Be, although repeating the calculations with a valence basis from the $2p^2$ state produced no significant change.

Table V shows the results of the same sequence of cal-

TABLE V. Total energies (in a.u.) and ionization energies (in 10^3 cm^{-1}) for Be and B^+, based on the minimal CSF reference set, set B.

Approximation	$2s^2\ ^1S$	$2s2p\ ^1P$	$2p^2\ ^1D$	$2p^2\ ^1S$	$2s3s\ ^1S$	$2s3d\ ^1D$	$2s2p\ ^3P$	$2p^2\ ^3P$	$1s^22s$
			Be total energy						
Referent CI	−14.616 82	−14.411 26	−14.355 33		−14.368 66	−14.324 59	−14.511 49	−14.336 29	−14.277 39
L (through i)	−14.619 22	−14.424 44	−14.360 00		−14.370 82	−14.326 04	−14.518 70	−14.345 71	
$L+KL$ (through i)	−14.624 34	−14.430 07	−14.364 53		−14.375 14	−14.330 48	−14.523 98	−14.351 44	−14.281 66
$L+KL+K$ (through h)	−14.666 81	−14.472 21	−14.407 47		−14.417 65	−14.373 13	−14.566 32	−14.394 41	−14.324 40
Relativistic $+l$ extrapolation	−14.669 36	−14.474 71	−14.409 89		−14.420 15	−14.375 61	−14.568 79	−14.396 80	−14.326 88
Davidson correction	−14.669 47	−14.475 21	−14.410 15		−14.420 35	−14.376 99	−14.569 11	−14.396 86	−14.326 91
			Be ionization energy						
Referent CI	−74.493	−29.380	−17.106		−20.031	−10.359	−51.376	−12.925	
L (through i)	−75.020	−32.272	−18.130		−20.503	−10.676	−52.959	−14.993	
$L+KL$ (through i)	−75.204	−32.570	−18.187		−20.514	−10.712	−53.179	−15.312	
$L+KL+K$ (through h)	−75.145	−32.437	−18.230		−20.464	−10.693	−53.092	−15.363	
Relativistic $+l$ extrapolation	−75.162	−32.443	−18.217		−20.469	−10.694	−53.091	−15.345	
Davidson correction	−75.179	−32.546	−18.267		−20.505	−10.990	−53.153	−15.351	
Experiment[a]	−75.192	−32.627	−18.310		−20.515	−10.764	−53.212	−15.497	
			B^+ total energy						
Referent CI	−24.296 36	−23.949 45	−23.819 83	−23.686 20	−23.668 70	−23.586 21	−24.120 15	−23.835 06	−23.375 97
L (through i)	−24.299 08	−23.961 61	−23.830 23	−23.715 75	−23.671 49	−23.595 15	−24.127 75	−23.844 66	
$L+KL$ (through i)	−24.305 86	−23.971 20	−23.838 70	−23.723 36	−23.678 28	−23.600 77	−24.135 65	−23.854 45	−23.381 32
$L+KL+K$ (through h)	−24.348 33	−24.013 73	−23.882 05	−23.766 07	−23.720 66	−23.643 27	−24.178 18	−23.897 81	−23.424 23
Relativistic $+l$ extrapolation	−24.355 17	−24.020 43	−23.888 43	−23.772 63	−23.727 33	−23.649 87	−24.184 80	−23.904 15	−23.430 81
Davidson correction	−24.355 23	−24.020 65	−23.888 64	−23.773 65	−23.733 04	−23.650 28	−24.184 99	−23.904 35	−23.430 83
			B^+ ionization energy						
Referent CI	−201.994	−125.859	−97.412	−68.084	−64.243	−46.141	−163.321	−100.753	
L (through i)	−202.590	−128.526	−99.694	−74.570	−64.856	−48.103	−164.988	−102.861	
$L+KL$ (through i)	−202.902	−129.456	−100.378	−75.065	−65.172	−48.160	−165.549	−103.834	
$L+KL+K$ (through h)	−202.807	−129.373	−100.476	−75.022	−65.056	−48.072	−165.464	−103.933	
Relativistic $+l$ extrapolation	−202.864	−129.401	−100.430	−75.018	−65.075	−48.075	−165.473	−103.881	
Davidson correction	−202.873	−129.445	−100.473	−75.235	−66.323	−48.160	−165.510	−103.921	
Experiment[b]	−202.887	−129.491	−100.524	−75.226	−65.909[c]	−48.201	−165.537	−103.960	

[a] See Ref. [10].

[b] See Ref. [11].

[c] See Ref. [19].

TABLE VI. Comparison of total-energy results (in a.u.) for the $2s2p\ ^3P$ and $2p^2\ ^3P$ states from SD SOC calculations using CSFs based on reference pair parent couplings and all possible couplings. Reference set B is used, which, in both instances, amounts to the single-configuration Hartree-Fock calculation.

Approximation	$2s2p\ ^3P$ Total number of CSFs	$2s2p\ ^3P$ Total energy	$2p^2\ ^3P$ Total number of CSFs	$2p^2\ ^3P$ Total energy
		Be		
Valence shell (i)	69	−14.518 70	38	−14.345 71
Parent coupled $KL(i)$	1410	−14.523 98	865	−14.351 44
All couplings $KL(i)$	2772	−14.523 99	1441	−14.351 44
Parent coupled $KL(i)+K(h)$	1621	−14.566 32	1060	−14.394 41
All couplings $KL(i)+K(h)$	4603	−14.566 35	3051	−14.394 41
		B^+		
Valence shell (i)	69	−24.127 75	38	−23.844 66
Parent coupled $KL(i)$	1410	−24.135 65	865	−23.854 45
All couplings $KL(i)$	2772	−24.135 67	1441	−23.854 45
Parent coupled $KL(i)+K(h)$	1621	−24.178 18	1060	−23.897 81
All couplings $KL(i)+K(h)$	4603	−24.178 20	3051	−23.897 82

culations based on the minimal reference set, set B of Table I. Not surprisingly, the computed energies are not as accurate as with set A, even though the reference set exceeds the Hartree-Fock configuration for every state, except the two triplets. The emphasis here too is on the ionization energies and transition energies. For neutral beryllium, before applying the Davidson correction, these calculations are worse than the previous ones by an amount ranging from 18 cm^{-1}, for the ground state, to 148 cm^{-1}, for $2s2p\ ^1P$. For B^+, the results are similar, sometimes better, sometimes worse. Enlarging the referent makes a difference of 163 cm^{-1} in the $2p^2\ ^1S$ state of B^+. The Davidson correction is larger, of course, but less reliable in those cases where it is needed the most, overshooting for the $2s3s$ state by about 400 cm^{-1}. This should not be surprising, since the correction was designed to estimate small "fine tuning" corrections. The importance of the $2p^2$ mixing in the $2s3s\ ^1S$ state is underscored by the fact that the minimal referent CI calculation, with only four CSFs, gives the wrong ordering of the energy levels. The result quoted for the reference CI energy for the $2s3s$ state of B^+ is therefore the second eigenvalue, not the third.

Just as in the earlier calculations, the core-correlation contributions of d and higher angular momentum substitution terms is essentially of no importance for ionization and excitation energies. Intershell-correlation contributions to the ionization energy, being significantly smaller to begin with, are affected much less by enlarging the reference set than those due to core correlation—the s and p contributions.

As discussed earlier, all pair substitution configurations are based on the parentage angular momentum couplings of the reference CSFs. One could also have made these pair substitutions including all possible angular momentum couplings as well as all possible orbital substitutions. To test the effect of doing so, the minimal referent, set B, calculations were repeated for the $2p^2\ ^3P$ and $2s2p\ ^3P$ states expanding the CSF basis to include all possible couplings for both the intershell-correlation terms as well as the core. The results of doing this are summarized in Table VI, which compares total energies calculated with parentage-coupled calculations with that of all possible couplings. The entries for K-shell correlation are obtained with all possible angular momentum couplings in both the intershell terms as well as the K shell. Not surprisingly, the effect is small, the largest energy shift being $\sim 6\ \text{cm}^{-1}$. The number of configurations generated, however, is much larger, by about a factor of 3. If one were tempted to evaluate a calculation simply by counting configurations, the all-coupling calculation would clearly be somewhat misleading. It should be noted, however, that these triplet terms present the worst case scenario. For the ground-state calculation, there would be the same number of CSFs in either the parent-coupled or unrestricted coupling schemes. The overall ^1S symmetry imposes a sufficiently strong constraint on the coupling possibilities to rule out any spuriously coupled terms.

RESULTS: OSCILLATOR STRENGTHS

Oscillator strengths were also calculated for all possible electric dipole transitions between the states treated here. The oscillator strength is given by the usual two forms

$$f_l=\frac{2}{3g_i}\Delta E|\langle\Phi_i|\mathbf{r}|\Phi_j\rangle|^2 \quad (\text{length}) \tag{7a}$$

and

$$f_v=\frac{2}{3g_i}\frac{1}{\Delta E}|\langle\Phi_i|\nabla|\Phi_j\rangle|^2 \quad (\text{velocity}) . \tag{7b}$$

Here g_i is the statistical weight of the initial state, ΔE is the transition energy (in a.u.), and the squared transition matrix element, the multiplet strength, is assumed to be summed over all degeneracies in both initial and final states. Oftentimes, one quotes the product of the g and the f value, which is symmetric with respect to the direction of the transition, a practice which is followed here. The two forms of the f value must agree when computed with the exact wave functions. They need not do so when computed with approximate functions and usually do not, in varying degrees. Agreement of length and velocity oscillator strengths, of course, is a necessary but not sufficient condition that the calculated values be correct. Since the length form emphasizes the outer regions of the atom where valence correlation corrections have the greatest effect, it is usually the one preferred, even though it differs significantly from the velocity. The velocity form tends to be somewhat more democratic in its sampling of the wave functions and therefore requires a more even-handed treatment of correlation in both the core and valence regions of the atom. Since the present calculations are directed at precisely this problem, it is here suggested that the relative agreement of these two forms of the f value be taken as some measure of the accuracy of the f-value calculations.

For a SOC wave function, Eq. (1), the multiplet strength is then given by

$$S_{ij}=|\langle\Phi_i|\mathbf{r}|\Phi_j\rangle|^2=\left|\sum_{n,m} c_{i,n}c_{j,m}\langle\Phi_{i,n}|\mathbf{r}|\Phi_{j,m}\rangle\right|^2 \qquad (8)$$

with a similar expression for the velocity form. It should be noted that, since each of the atomic states are computed variationally and independnetly of each other, the many electric dipole matrix elements of Eq. (8) over the CSFs involve determinants of overlap integrals of the basis orbitals of the two states, as well as "virtual" dipole contributions arising from the nonorthogonality of these orbitals. Since the present calculations are all based on angular momentum projected determinantal wave functions, including fully such contributions to the matrix elements was therefore quite straightforward and was done so for all the calculations reported here, even though the effect is not very large in an atom such as beryllium, where there are only two electrons outside a $1s^2$ core, which is virtually unchanged from state to state.

The results for the gf values obtained with the various levels of approximation, in exactly the same form as the energy results, are shown in Tables VII (Be) and VIII (B^+). In every case the experimental transition energy is used in computing gf, which then throws the burden of the accuracy of the calculation fully on the theoretical value of the multiplet strength. Several observations can be made with regard to these results.

Usually, the addition of intershell correlation quickly brings the velocity form into good agreement with the length calculation, which in turn is changed much less from the valence-shell-only calculation. While adding the core correlations through p-symmetry terms makes a

TABLE VII. Theoretical gf values for Be.

Approximation	Transition λ (Å)	$2s^2\,{}^1S$–$2s2p\,{}^1P$ 2349.4	$2s2p\,{}^1P$–$2p^2\,{}^1D$ 6984.7	$2s2p\,{}^1P$–$2s3s\,{}^1S$ 8256.3	$2s2p\,{}^1P$–$2s3d\,{}^1D$ 4573.9	$2s2p\,{}^3P$–$2p^2\,{}^3P$ 2651.5
			Reference set A			
Referent CI	length	1.3657	0.0000	0.3501	1.0057	4.0624
	velocity	1.4940	0.0004	0.3550	0.8864	4.3533
L shell (d)	length	1.3897	0.0031	0.3753	1.2206	4.0563
	velocity	1.4585	0.0011	0.3598	1.2052	4.3335
L shell (g)	length	1.3923	0.0024	0.3710	1.2320	4.0755
	velocity	1.4543	0.0006	0.3612	1.2339	4.2983
L shell (i)	length	1.3925	0.0022	0.3702	1.2332	4.0758
	velocity	1.4539	0.0005	0.3616	1.2373	4.2977
$L(i)+KL(d)$	length	1.3743	0.0010	0.3596	1.2195	4.0094
	velocity	1.3780	0.0011	0.3497	1.2029	4.0229
$L(i)+KL(i)$	length	1.3734	0.0007	0.3586	1.2201	4.0076
	velocity	1.3773	0.0008	0.3498	1.2046	4.0195
$L(i)+KL(i)+K(p)$	length	1.3756	0.0001	0.3560	1.2030	4.0228
	velocity	1.3769	0.0000	0.3504	1.1809	4.0154
$L(i)+KL(i)+K(h)$	length	1.3755	0.0000	0.3559	1.2011	4.0232
	velocity	1.3775	0.0000	0.3503	1.1784	4.0173
			Reference set B			
Referent CI	length	1.3394	0.0036	0.3581	0.8822	4.7944
	velocity	1.4840	0.0124	0.3767	2.8773	3.2064
$L(i)+KL(d)$	length	1.3737	0.0010	0.3575	1.2123	4.0115
	velocity	1.3808	0.0011	0.3520	1.2003	4.0136
$L(i)+KL(i)$	length	1.3728	0.0007	0.3567	1.2129	4.0103
	velocity	1.3802	0.0008	0.3524	1.2016	4.0083
$L(i)+KL(i)+K(p)$	length	1.3752	0.0002	0.3612	1.1918	4.0809
	velocity	1.3810	0.0001	0.3614	1.1677	3.9198
$L(i)+KL(i)+K(h)$	length	1.3751	0.0002	0.3616	1.1900	4.0865
	velocity	1.3817	0.0001	0.3621	1.1654	3.9138

small change, just as with the energy difference calculations, higher-symmetry core correlations introduce a negligible alteration in the f value. In general, length and velocity forms agree to within 1%, the largest disagreements being about 2% for the transitions involving $2s3s$ and $2s3d$ in neutral beryllium. It is suggested here that one should adopt the length value with an uncertainty of perhaps twice the l-v discrepancy. The f-value calculations are not as sensitive to the choice of reference set as the energy results, which suggests that for more complex systems it may not be so important to make the SOC expansion quite so exhaustive. The only exception is the triplet transition $2s2p$-$2p^2$ in neutral beryllium where, for some reason, the minimal referent final SOC still shows a l-v discrepancy of 4%. As soon as one moves to the singly ionized isoelectronic ion, the l-v disagreement falls well below 1% for all cases, which is encouraging for ionic f-value calculations.

The $2s2p\ {}^1P-2p^2\ {}^1D$ transition in Be and the $2s2p\ {}^1P-2s3s\ {}^1S$ transition in B^+ are both notable for the almost total mutual cancellation of the contributions to the transition moment of the dominant CSFs in the wave function, resulting in essentially zero oscillator strengths. With the ensuing loss in significant figures of so much of the multielectron integrand, it is difficult, if not impossible, to assign any accuracy to the resulting theoretical values, irrespective of any putative agreement or disagreement with experiments. In the case of the $2s2p$-$2s3s$ transition in B^+, the weakness of the transition probably rules out the use of this transition for determining the experimental position of the ${}^1S$ level. We note also the fact that the minimal referent CI calculation alone gives f values that bear no resemblance whatever to the final result, even though the length and velocity values agree reasonably well.

These gf-value calculations are compared with experimental [18,19] and other theoretical results in Table IX. Here, only those calculations which attempt to include explicitly either intershell- or core-correlation corrections are included for comparison. The variational r_{12} calculation was the first accurate treatment of core effects and is potentially the most accurate [20]. However, considerable restrictions in the number and types of terms had to be invoked to keep the calculation manageable. The CI calculations of Hibbert [21] consisted of a set of calculations of successively longer expansion lengths, with selected intershell CSFs being included only for the shorter ones. The correction so obtained, however, was then applied to the most complete valence-shell calculation. The CI calculations of Moccia and Spizzo [22] are STO-based, large valence-shell calculations with selected intershell correction terms added. The Bethe-Goldstone calculation [23] is essentially a sequence of two-particle CI calculations where the various pair contributions are

TABLE VIII. Theoretical gf values for B^+.

	Transition	$2s^2\ {}^1S-2s2p\ {}^1P$	$2s2p\ {}^1P-2p^2\ {}^1D$	$2s2p\ {}^1P-2s3s\ {}^1S$	$2s2p\ {}^1P-2s3d\ {}^1D$	$2s2p\ {}^1P-2p^2\ {}^1S$	$2s2p\ {}^3P-2p^2\ {}^3P$
Approximation	λ (Å)	1362.5	3452.2	1572.8	1230.2	1842.8	1624.0
			Reference set A				
Referent CI	length	0.9937	0.4963	0.0075	1.6813	0.6753	3.1178
	velocity	1.1067	0.5416	0.0091	1.6670	0.7379	3.3970
L shell (d)	length	1.0129	0.4773	0.0051	1.5873	0.6878	3.1196
	velocity	1.0878	0.5008	0.0058	1.5450	0.7161	3.3917
L shell (g)	length	1.0146	0.4834	0.0037	1.5974	0.6902	3.1275
	velocity	1.0824	0.5088	0.0040	1.5732	0.7169	3.3690
L shell (i)	length	1.0147	0.4843	0.0032	1.5980	0.6906	3.1277
	velocity	1.0816	0.5117	0.0034	1.5761	0.7155	3.3685
$L(i)+KL(d)$	length	1.0001	0.4839	0.0006	1.5562	0.6786	3.0798
	velocity	1.0024	0.4830	0.0007	1.5456	0.6777	3.0857
$L(i)+KL(i)$	length	0.9991	0.4842	0.0005	1.5528	0.6782	3.0784
	velocity	1.0009	0.4814	0.0006	1.5459	0.6771	3.0818
$L(i)+KL(i)+K(p)$	length	0.9997	0.4873	0.0002	1.5591	0.6793	3.0846
	velocity	0.9996	0.4855	0.0003	1.5557	0.6763	3.0801
$L(i)+KL(i)+K(h)$	length	0.9997	0.4874	0.0002	1.5597	0.6793	3.0847
	velocity	1.0001	0.4861	0.0003	1.5567	0.6764	3.0816
			Reference set B				
Referent CI	length	0.9903	0.4584	0.2590	1.6789	0.5584	3.4857
	velocity	1.1137	0.3605	0.2258	1.6894	0.8107	2.4909
$L(i)+KL(d)$	length	0.9997	0.4835	0.0006	1.5539	0.6778	3.0803
	velocity	1.0024	0.4825	0.0007	1.5460	0.6776	3.0794
$L(i)+KL(i)$	length	0.9987	0.4838	0.0005	1.5505	0.6774	3.0792
	velocity	1.0009	0.4808	0.0006	1.5462	0.6772	3.0743
$L(i)+KL(i)+K(p)$	length	0.9996	0.4858	0.0004	1.5515	0.6787	3.0996
	velocity	1.0000	0.4809	0.0005	1.5495	0.6744	3.0387
$L(i)+KL(i)+K(h)$	length	0.9996	0.4858	0.0004	1.5516	0.6787	3.1012
	velocity	1.0006	0.4811	0.0005	1.5499	0.6744	3.0366

TABLE IX. Comparison of gf values calculated here with experiment and other calculations.

Transition		Present	Variational (r_{12})[a]	CI (Hibbert)[b]	CI (Moccia and Spizzo)[c]	Bethe-Goldstone[d]	Expt.	Sequence analysis[e]
				Be				
$2s^2\,{}^1S-2s2p\,{}^1P$	length	1.376	1.344	1.371	1.385	1.386	1.341 ± 0.051[f]	1.341 ± 0.047
	velocity	1.378		1.377	1.331	1.378		
$2s2p\,{}^1P-2s3s\,{}^1S$	length	0.356			0.360			
	velocity	0.350			0.370			
$2s2p\,{}^1P-2s3d\,{}^1D$	length	1.201			1.204			
	velocity	1.178			1.215			
$2s2p\,{}^3P-2p^2\,{}^3P$	length	4.023		4.068	4.042	4.048		
	velocity	4.017		4.050	3.704	4.007		
				B^+				
$2s^2\,{}^1S-2s2p\,{}^1P$	length	1.000		1.021		1.013	0.971 ± 0.079[g]	0.965 ± 0.020
	velocity	1.000		0.998		1.009		
$2s2p\,{}^1P-2p^2\,{}^1S$	length	0.679		0.690			0.72 ± 0.06[g]	
	velocity	0.676		0.699				
$2s2p\,{}^1P-2p^2\,{}^1D$	length	0.487		0.483				
	velocity	0.486		0.501				
$2s2p\,{}^3P-2p^2\,{}^3P$	length	3.085		3.132			3.07 ± 0.16[g]	
	velocity	3.082		3.141				

[a] Sims & Whitten [20].
[b] Hibbert [21].
[c] Moccia and Spizzo [22].
[d] Moser, Nesbet, and Gupta [23].
[e] Reistad and Martinson [24].
[f] Martinson, Gaupp, and Curtis [18].
[g] Bashkin *et al.* [19].

computed independently and then combined for the final result.

With the exception of the velocity value of Moccia and Spizzo, all the calculations are within 3% of each other and agree with the experiments to within the experimental uncertainties. The marginal exception to this involves the resonance line f value of B^+ obtained by Reistad and Martinson [24] by smoothing the data for the isoelectronic sequence in an attempt to reduce the error bars for the entire sequence. The internal consistency of the present data and the agreement with most of the other calculations suggest that the experiments may be a bit low for the resonance transitions in Be and B^+. As a rule, the somewhat *ad hoc* correction procedure of Hibbert seems to work rather well and this approach should probably be explored further.

CONCLUSIONS

The calculations described here indicate that, for purposes of accurately computing oscillator strengths and valence-shell transition energies, a complete treatment of core correlations is unnecessary, that is, for an accuracy of about 1% for f values and 10–50 cm^{-1}, i.e., 0.005 eV, for energy differences. It is important, especially for transition energies, to include core correlations through the primary occupied valence-shell symmetries in a fairly complete manner, i.e., the K-shell semi-internal or "interference" terms in the SOC trial function. The slowly convergent, higher-symmetry core terms have no effect on f values and, to within 1–2 cm^{-1}, cancel out in all energy differences. Another redundancy which unnecessarily expands the size of the SOC expansion significnatly pertains to the angular momentum couplings of the pair substitution configurations. Only those terms coupled in the same way as the fractional parentage of the reference configurations make a contribution of any significance to either f values or transition energies.

All the calculations reported here have involved single- and double-substitution configurations in the wave-function expansion, but with reference to a multiconfiguration set of configuration-state functions. Single referent, Hartree-Fock SD calcultions have long been known to suffer from their inability to adequately account for the cancellation of unlinked diagram terms in a perturbation expansion of the wave function. In a variational SOC calculation this cancellation is accomplished by including triple- and quadruple- and higher, substitution CSFs. The present results indicate that a SD calculation, when based on a carefully chosen multiconfiguration reference set, appears to account for the bulk of this shortfall. It is important to throw as much of the correlation as possible into the reference set, the most general way being to use a referent obtained from a multiconfiguration Hartree-Fock, or multiconfiguration self-consistent field, calculation. The present work suggests that the reference set should constitute something like 99% of the final wave function. At this point, the residual corrections are small enough that estimation procedures such as the Davidson correction can account for a significant part of the remaining discrepancy in the energy. It is most likely that the remaining transition energy discrepancies arise from the unaccounted for triple- and quadruple-substitution terms.

The $2s3s\ ^1S$ state of singly ionized boron stands out for the large disagreement between theory and experiment. It is not clear how to improve the calculations sufficiently to remove the discrepancy. The same state in neutral beryllium is calculated quite well, as is the $2p^2\ ^1S$ state of B^+. In this case, this is the third ^1S state, which conceivably might have something to do with the problem, although the multiconfiguration reference set was enlarged in such a way as to account for this situation. As of this writing, this anomaly remains.

While the multiconfiguration referent is important for accurately calculating oscillator strengths, it is much less so than for the energies. In general, the length form of the f value has already converged with a valence-shell-only-correlation calculation. Intershell correlations, and to a lesser extent core correlation, serve mainly to bring the velocity form into agreement with the length result. The length form oscillator strengths all appear to be accurate to within 1–2 %. The exceptions, of course, are the large configuration cancellation cases, the $2s2p\ ^1P-2p^2\ ^1D$ transition in beryllium and the $2s2p\ ^1P-2s3s\ ^1S$ transition in B^+, where the cancellation is so complete that it is not possible to say much about the f value at all. It should be noted that, in both these cases, the calculations using only the minimal reference set CSFs yield wildly erroneous f values and, in the B^+ case, length and velocity values which even agree reasonably well.

It is, of course, somewhat risky to generalize from these results to atomic calculations in general. Probably, one will find the same general qualitative behavior of correlation contributions to energy differences and f values for most first row atoms and ions. The state-dependent semi-internal core-correlation effect will probably diminish significantly for atoms on the right-hand side of the Periodic Table, since the $2s$ and $2p$ orbitals are usually at or near full occupancy. While it is tempting to extend these ideas to the second or third row atoms, the larger occupancy and more diffuse nature of the core would make such speculation, at best, unwise.

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APPENDIX

Table X shows the K-shell correlation basis derived from SOC calculations on the ground state of the heliumlike ions Be^{2+} and B^{3+}. The basis sets utilized two ζ's for each symmetry, with the principal quantum numbers running from a starting value to some maximum. This is indicated in the tables by the notation n_1-n_2, which means the set of STOs with the given ζ and principal quantum numbers $n_1, n_1+1, \ldots, n_2$. Such an arrangement reduces the variational calculation to a two-parameter optimization for each orbital symmetry, just as the "even-tempered" basis set approach does. Even-tempered sets were also investigated and found to give essentially the same accuracy as the current double ζ ones, but with a somewhat greater tendency towards linear dependence. In both cases, as the sets were enlarged, linear dependence became a problem, slightly more so for the even-tempered sets.

TABLE X. K-shell basis set of Slater-type orbitals obtained from calculations of the ground state of the heliumlike ions. Column 1 gives the principal quantum numbers as defined in Eq. (3) of the text. Columns 2 and 3 show the corresponding values of the nonlinear parameters ζ. Total energies are given in a.u.

Principal quantum numbers	Be^{2+}	B^{3+}
$2s$	7.7	9.8
$2s$-$3s$	10.9	13.4
$2p$	5.15	6.6
$2p$-$5p$	12.3	15.6
$3d$	6.72	8.55
$3d$-$6d$	15.1	19.1
$4f$	8.9	11.3
$4f$-$6f$	16.3	20.6
$5g$	10.9	13.8
$5g$-$7g$	18.9	23.9
$6h$	13.6	17.3
$6h$-$7h$	20.0	25.2
$7i$-$8i$	19.0	24.0
E_{total}	$-13.655\,312$	$-22.030\,697$
E_{exact} [a]	$-13.655\,566$	$-22.030\,973$

[a] See Ref. [25].

The computed total energies are also given and compared with the exact nonrelativistic values from highly accurate r_{12} calculations [25]. A significant part of the energy discrepancy is a consequence of truncating the harmonic series at $l=6$, i.e., i orbitals. This basis set was used for the core and core-valence correlation of all states of Be (and B^+). The correlation orbitals were obtained from a natural-orbital transformation of the heliumlike ground-state wave function. To obtain the beryllium atom correlation orbitals, these orbitals were appended to the valence set, sequentially Schmidt orthogonalizing them to the valence orbitals. The entire orbital set was then used to represent core and core-valence correlations. Finally, it should be noted that Table X gives only the correlation basis. Thus, for s functions, the basis actually consisted of the three STOs given here plus the ground-state Hartree-Fock set.

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