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Superposition of Configurations and Atomic Oscillator Strengths – Boron Isoelectronic Sequence*

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Oscillator strengths have been computed for transitions between a number of low-lying levels in B I and Ne VI. The wave functions were computed by the method of superposition of configurations, utilizing the pseudonatural orbital technique to accelerate convergence. The asymptotic limiting large-Zf values were also computed, using the nuclear charge perturbation expansion. Together with previous theoretical data from C II, these results have been used to make a graphical study of the f-value behavior for these transitions along the isoelectronic sequence. Comparisons were made between experiment and the predictions of the Hartree-Fock and charge-expansion methods as well as the present calculations. Finally, these theoretical curves were used to predict individual f values for each member of the sequence through $Z=15$ (P XI).

I. INTRODUCTION

The calculations reported here were undertaken to explore systematically, and on a uniformly accurate level of approximation, the behavior of atomic oscillator strengths along an isoelectronic sequence. These calculations arose naturally in response to several problems encountered in a recent, and more general, study of regularities in atomic f values.[1] One of these difficulties came from the heterogeneous level of accuracy of the data available for any given sequence, suggesting the desirability of studying a particular sequence at a uniformly good level of accuracy, say 20–30%. Another problem concerned the scarcity of reliable f-value data for the middle stages of ionization, it being presumed that the charge-expansion method[2] would be adequate for highly ionized species.

The plan of this paper, in brief, is the following. Moderately accurate variational calculations, using the method of superposition of configurations (SOC), are done on several of the ions in the boron sequence, namely, B I, C II, and Ne VI, and these calculations will be described in Sec. II. f values were then computed for the infinite Z limit of the conventional perturbation theory expansion,[2] including the zeroth-order degeneracies; this is discussed in Sec. III. The results of these two sets of calculations are combined in Sec. IV in a comprehensive study of the entire sequence by graphical methods. These theoretical curves are then used to predict the f values for the entire sequence through P XI.

The boron sequence was selected for a variety of reasons, not the least of which was theoretical convenience. With three electrons outside a compact K-shell core, the ions of this sequence are sufficiently simple that reasonably accurate calculations can be done with relative ease. Furthermore, while such a three-electron spectrum is fairly simple, it is still complex enough to show interesting configuration interaction effects in addition to the usual residual correlation corrections. Also, the calculations on C II had already been done earlier, which somewhat lightened the present computing burden. Finally, this sequence is one of the most favorable from the standpoint of the availability of good quality experimental f-value data for intermediate stages of ionization, largely from recent lifetime measurements by the phase shift and beam-foil techniques.[3-6] While the experimental data are still somewhat sparse, there are still enough to provide a reasonably adequate check on the predictions.

II. SOC CALCULATIONS FOR B I and Ne VI

Variational SOC wave functions were computed for the ground and a number of excited states of B I and Ne VI, utilizing the pseudonatural orbital (PSNO) technique to obtain rapid convergence. These wave functions are of the form,

$$\Phi = C_0\Phi_0 + \sum_{i,a} C_a{}^i \Phi_a{}^i + \sum_{i,j} \sum_{a,b} C_{ab}{}^{ij} \Phi_{ab}{}^{ij} + \cdots \quad . \tag{1}$$

Here, Φ_0 is the antisymmetrized product, single-configuration function appropriate for the state under consideration, and, in all the calculations described here, it is taken to be the Hartree-Fock wave function. Φ_0 is normally the dominant configuration in the SOC wave function. The correction configurations $\Phi_a{}^i$ are formed by replacing the orbital a, occupied in the Hartree-Fock function, by some "virtual" orbital i, and with the resulting function suitably projected to give a pure LS-coupling state. The double substitution terms $\Phi_{ab}{}^{ij}$ are obtained in a similar way. The coefficients in (1) are determined variationally, and they turn out to be the eigenvector elements of the usual energy-matrix eigenvalue equation.

The Hartree-Fock wave functions were computed by the analytical expansion method technique using the University of Chicago self-consistent field program for the IBM 7094 computer.[7] The basis functions for the expansion method Hartree-Fock orbitals were the usual Slater-type orbitals (STO), with the exponents suitably optimized to minimize the total energy.

The crux of the SOC method lies in the choice of the virtual orbitals to use in the expansion (1), and the PSNO procedure adopted here has been described in detail elsewhere.[8,9] Briefly, the procedure is the following. One selects a single electron pair which spans, reasonably well, the spatial extent of the electrons to be correlated, and does an exhaustive SOC calculation on just this pair. A natural orbital transformation[10] is then carried out on this SOC wave function to determine a set of rapidly converging virtual orbitals, PSNO's. In effect, one calculates the natural orbital expansion for this pair of electrons in the Hartree-Fock field of the rest of the atom. It has turned out that these PSNO's are then also very effective for representing the correlations of other pairs of electrons with approximately the same radial distribution. For instance, for the ground state of boron $2s^2 2p\ ^2P$, the PSNO's were determined for the $2s2p\ ^1P$ pair, and these orbitals were then used to correlate other pairs, such as $2s^2\ ^1S$ and $2s2p\ ^3P$.

The total energy results obtained for the ground states of boron and neon are given in Table I.[11] The notation referring to $n = 3$ configurations, etc., means all configurations have been included in the wave functions which contain $3s$, $3p$, or $3d$ orbitals and which have been found to be energetically significant. The principal quantum-number labeling follows the ordering of the orbitals as they come out of the PSNO transformation, and it should thus represent an approximate ordering of the PSNO's according to their correlation importance. As a further illustration of the nature of these calculations the coefficients of the largest ground-state SOC wave functions are given in the Appendix.

As with both C I and II, the most important single configuration involved the substitution, $2s^2 \rightarrow 2p^2$, which for boron is the $2p^3$ term. Here too, moreover, the next most important configuration was a spin-polarization term involving only a single space-orbital substitution, namely, the $(2p3d\ ^1P)2s$ configuration. For neutral boron, this one configuration picked up 0.018 a.u. of the correlation energy (≈ 0.5 eV).

As can be seen from Table I, the K shell has been left alone, and the K-L intershell correlation has been neglected. This has also been done for all the excited states, the idea being that with the K-shell electrons represented by a Hartree-Fock distribution, only the L-shell electrons should be important for spectroscopic properties such as energy levels and f values. The computed L-shell correlation energy for the boron ground state of 0.068 a.u. compares favorably with several other recent calculations. A straightforward multi-configuration calculation by Schaefer and Harris[12] has given 0.066 a.u., and an adaptation of the Bethe-Goldstone procedure by Nesbet[13] has obtained 0.071 a.u.

Various excited states for B I and Ne VI were also calculated in exactly the same way as the ground states. Each state was computed independently of all the others, with parameters varied and configurations added to depress the total energy as much as possible. The way in which these states have settled into place, relative to the computed ground state, is shown in Table II and compared with the experimental energy levels.[14] It can be seen that the agreement between the experimental and theoretical energy-level spectra is quite good, especially considering the fact that these are completely *ab initio* calculations. The largest discrepancy for boron is about 450 cm^{-1}. While there are two discrepancies of about 2000 cm^{-1} for Ne VI, these are for the quartet levels for which the experimental positions are somewhat uncertain, intersystem transitions being unknown for this ion. The heretofore unobserved $2p^3\ ^2D$ term in Ne VI is predicted to lie about 357 500

TABLE I. Computed total energies and L-shell correlation energies (in a.u.) for the ground states of B I and Ne VI.

Wave-function type	B I No. of config.	B I Total energy	B I Correlation energy	Ne VI No. of config.	Ne VI Total energy	Ne VI Correlation energy
Hartree-Fock	1	−24.52906	0.0	1	−115.9108	0.0
$2s^2 2p + 2p^3$	2	−24.55944	0.0304	2	−115.9815	0.0707
All $n=3$ config.	17	−24.59332	0.0643	14	−116.0187	0.1079
All $n=4$ config.	35	−24.59750	0.0684	27	−116.0252	0.1144

TABLE II. Computed and observed term energies (in a.u.) for neutral boron and neon VI.

Term	No. of config.	Hartree-Fock	SOC	Observed[a]
		B I		
$2s^22p\ ^2P$	35	0.0	0.0	0.0
$2s2p^2\ ^4P$	16	0.0784	0.1293	0.1313
$2s^23s\ ^2S$	25	0.1770	0.1818	0.1824
$2s2p^2\ ^2D$	45	0.2172	0.2202	0.2180
$2s^23p\ ^2P$	35	0.2128	0.2205	0.2215
$2s^23d\ ^2D$	31	0.2353	0.2480	0.2495
$2p^3\ ^4S$	8	0.4010	0.4420	0.4421
		Ne VI		
$2s^22p\ ^2P$	27	0.0	0.0	0.0
$2s2p^2\ ^4P$	10	0.3521	0.4485	0.4571
$2s2p^2\ ^2D$	38	0.7624	0.8105	0.8116
$2s2p^2\ ^2S$	31	0.9914	1.0491	1.0479
$2s2p^2\ ^2P$	22	1.1091	1.1376	1.1344
$2p^3\ ^4S$	5	1.3668	1.4532	1.4624
$2p^3\ ^2D$	23	1.5974	1.6291	
$2p^3\ ^2P$	34	1.7499	1.8444	1.8461
$2s^23s\ ^2S$	25	3.3157	3.2852	3.2885
$2s^23p\ ^2P$	29	3.5452	3.5115	3.5111
$2s^23d\ ^2D$	35	3.7320	3.7140	3.7159

[a] See Ref. 11.

cm^{-1} above the ground state.

The oscillator strengths for the allowed electric dipole transitions among these states have been computed, in both the dipole-length and velocity forms, and are shown in Tables III and IV. The length and velocity forms of the oscillator strength for a transition from state ψ to ψ' are given by

$$f_L = \tfrac{2}{3}(E - E')g^{-1}\,|\langle\psi|r|\psi'\rangle|^2\ , \tag{2}$$

$$f_V = \tfrac{2}{3}(E - E')^{-1}g^{-1}\,|\langle\psi|\nabla|\psi'\rangle|^2\ , \tag{3}$$

where g is the statistical weight of the initial state, and the squared matrix elements (multiplet strengths) are assumed to be summed over any degeneracies in both the initial and final states. Both these forms must agree if exact wave functions and energies are used, but they need not, and usually do not, for approximate wave functions. Agreement between them, using approximate wave functions, is, furthermore, only a necessary and not sufficient condition for the correctness of the f value. Nevertheless, in view of the accuracy of the computed energy-level spectrum and since the basic model (SOC) is an open-ended one, capable of converging to any desired accuracy on the exact wave functions, the agreement between f_L and f_V should provide some handle on assessing the accuracy of the calculations.

In the following sections of this paper, somewhat

TABLE III. Theoretical and experimental oscillator strengths for neutral boron.

Transition	λ(Å)	Hartree-Fock		SOC		Experiment
		length	velocity	length	velocity	
$2s^22p\ ^2P-2s^23s\ ^2S$	2498	0.052	0.063	0.067	0.074	0.055[a]
$2s^22p\ ^2P-2s2p^2\ ^2D$	2090	0.339	0.336	0.067	0.084	0.059,[a] 0.048[b]
$2s^22p\ ^2P-2s^23d\ ^2D$	1825	0.109	0.092	0.197	0.189	0.175[b]
$2s^23s\ ^2S-2s^23p\ ^2P$	11650	1.269	0.995	1.199	0.978	
$2s^23p\ ^2P-2s^23d\ ^2D$	16270	1.036	0.691	0.786	0.765	
$2s2p^2\ ^4P-2p^3\ ^4S$	1466	0.266	0.146	0.213	0.225	

[a] See Ref. 6.

[b] See Ref. 3.

TABLE IV. Theoretical oscillator strengths for Ne VI. The wavelengths in brackets are theoretical.

Transition	λ(Å)	Hartree-Fock		SOC	
		length	velocity	length	velocity
$2s^22p\ ^2P$-$2s2p^2\ ^2D$	561	0.143	0.133	0.091	0.098
$2s^22p\ ^2P$-$2s2p^2\ ^2S$	435	0.037	0.022	0.050	0.055
$2s^22p\ ^2P$-$2s2p^2\ ^2P$	402	0.356	0.155	0.254	0.272
$2s^22p\ ^2P$-$2s^23s\ ^2S$	139	0.027	0.030	0.026	0.028
$2s^22p\ ^2P$-$2s^23d\ ^2D$	123	0.533	0.503	0.569	0.562
$2s2p^2\ ^2D$-$2p^3\ ^2D$	[557]	0.130	0.121	0.111	0.125
$2s2p^2\ ^2D$-$2p^3\ ^2P$	440	0.055	0.033	0.074	0.080
$2s2p^2\ ^2S$-$2p^3\ ^2P$	571	0.171	0.171	0.106	0.120
$2s2p^2\ ^2P$-$2p^3\ ^2D$	[927]	0.134	0.273	0.103	0.034
$2s2p^2\ ^2P$-$2p^3\ ^2P$	640	0.117	0.118	0.143	0.142
$2s^23s\ ^2S$-$2s^23p\ ^2P$	2047	0.499	0.521	0.416	0.386
$2s^23p\ ^2P$-$2s^23d\ ^2D$	2225	0.243	0.207	0.203	0.198
$2s2p^2\ ^4P$-$2p^3\ ^4S$	453	0.105	0.067	0.096	0.108

more emphasis will be given to the dipole-length form of the f value. In the first place, most of the transitions discussed here do not involve a drastic change in the electronic charge distribution, such as might occur for a transition to a high-lying Rydberg state. In such cases, the dipole-length integrand is large just in those regions of space where the wave functions are large,[9] so that f_L should be at least as good as f_V for variational functions. Furthermore, since the velocity form puts more emphasis on the K-shell and K-L intershell aspects of the wave function, which are not correlated in the present work, it is reasonable to expect the dipole-length form to include more of the correlation corrections and thus be more reliable.

With these thoughts in mind then, one can turn to the results of Tables III and IV. The experimental determinations are lifetime measurements which have an uncertainty of ≃ 10%, and it can be seen that the SOC dipole-length f varies are in reasonably good agreement, especially if one assigns an uncertainty of 25% to the calculated values. The degree of convergence of the f values, as more configurations are sequentially added to the Hartree-Fock function, also supports an accuracy assignment in this range. The drastic change for the $2s^22p\ ^2P$ – $2s2p^2\ ^2D$ transition in boron in going from the Hartree-Fock to SOC and experiment should be noted in particular. This is due to the effect of adding configurations of the form $2s^2nd$ to $2s2p^2$, i.e., the admixture of the higher-lying Rydberg series. There is no experimental data for Ne VI, but one feature that should be noted is the relatively small difference between the Hartree-Fock and presumably more accurate SOC f values. We will return to this point in discussing the isoelectronic sequence as a whole.

III. ASYMPTOTIC LARGE-Z LIMIT

The perturbation expansion of atomic properties, in descending powers of the nuclear charge Z, has a long history beginning with the pioneering work of Hylleraas,[15] and has been reemphasized in recent times by various workers. The basic theory will only be sketched here, since a more detailed exposition is available in the more general study of f-value regularities by Wiese and Weiss.[1]

The usual perturbation approach[2, 15–17] is to scale all distances by Z, $r \rightarrow Zr$, which enables one to treat the entire interelectronic repulsion part of Schrödinger's equation as a perturbation, with Z^{-1} as the perturbation parameter. The zeroth-order Hamiltonian for this separation is then simply a sum over one-electron hydrogenic Hamiltonians, and one has the following expansions for the wave function and energy:

$$\psi = \psi_0 + \psi_1 Z^{-1} + \psi_2 Z^{-2} + \cdots, \tag{4}$$

$$E = \epsilon_0 Z^2 + \epsilon_1 Z + \epsilon_2 + \epsilon_3 Z^{-1} + \cdots. \tag{5}$$

Here, ψ_0 is an antisymmetrized product of hydrogen-atom orbitals, and ϵ_0 is simply the sum, over the electrons, of the hydrogen-atom energies. The first-order energy ϵ_1, if there is no zeroth-order degeneracy, is given by

$$\epsilon_1 = \langle \psi_0 | V | \psi_0 \rangle, \tag{6}$$

where V, the perturbation, is a sum over all the electrons of the interelectronic interaction

$$V = \sum_{\mu > \nu} r_{\mu\nu}^{-1}. \tag{7}$$

The existence of a degeneracy in zeroth order means that there is a set of zeroth-order functions $[\psi_0^j]$, all with the same ϵ_0, and one must then compute ϵ_1 by diagonalizing the first-order perturbation matrix,

$$V_1^{ij} = \langle \psi_0^i | V | \psi_0^j \rangle \ . \tag{6$'$}$$

This determines a linear combination of the $[\psi_0^j]$ which is then the appropriate zeroth-order wave function. A typical example of this would be the ground state of berylliumlike ions, $2s^2\ {}^1S$, which is asymptotically degenerate with $2p^2\ {}^1S$.

Substituting (4) and (5) into the expression for f_L [Eq. (2)] leads to the oscillator-strength expansion

$$f = f_0 + f_1 Z^{-1} + f_2 Z^{-2} \ldots \ , \tag{8}$$

where the leading term

$$f_0 = \tfrac{2}{3}\, \Delta\epsilon_0 g^{-1}\, |\langle \psi_0 | r | \psi_0' \rangle|^2 \ , \tag{9}$$

is the oscillator strength computed with purely hydrogenic functions. If there is a zeroth-order degeneracy for either of the states in the transition, of course, one must use the zeroth-order linear combination arising from the diagonalization of (6′). If, furthermore, there is no change in the principal quantum numbers in the transition, e.g., $2s^2 2p - 2s2p^2$, then ϵ_0 does not change, f_0 vanishes and (8) becomes

$$f = \bar{f}_1 Z^{-1} + \bar{f}_2 Z^{-2} + \cdots \ , \tag{10}$$

where
$$\bar{f}_1 = \tfrac{2}{3}\Delta\epsilon_1 g^{-1} |\langle \psi_0 | r | \psi_0' \rangle|^2 \ . \tag{11}$$

These considerations have several consequences. In the first place, they suggest that Z^{-1} is the natural parameter against which to plot f values in a graphical display of the isoelectronic sequence. The entire sequence is then compressed in the region between $Z^{-1} = 0$ and the value for the neutral atom. Secondly, one can calculate relatively easily the way in which these curves start at the zero end, either the initial value f_0 or, if this vanishes, then the slope of the curve at the origin. It is the calculation of these asymptotic limits for the boron sequence which is displayed in Tables V and VI.

Table V gives the zeroth- and first-order energies for the relevant states of the boron sequence. For the n^3 states ($2s^2 2p$, $2s2p^2$, etc.) the results agree with those of Linderberg and Shull.[17] In those cases of zeroth-order degeneracy, all possible degenerate configurations have been included in the diagonalization of the first-order matrix, which is not always a completely trivial matter. Thus, for example, the zeroth-order wave function for $2s^2 3d$ included the configurations $(2s2p\ {}^3P)3p$, $(2s2p\ {}^1P)3p$, $3s2p^2$, $(2p^2\ {}^1D)3d$, $(2p^2\ {}^3P)3d$, and $(2p^2\ {}^1S)3d$. The corresponding results for the f values are given in Table VI, where we have tabulated either the limiting value f_0 [Eq. (9)], or, for the $n \to n$ transitions, the asymptotic slope of the f-value curve $\bar{f}_1$ [Eq.(11)]. Also included in this table are the "incorrect" single-configuration values which are obtained by leaving out the mixing of the zeroth-order degenerate configurations, and which represent the large-Z limits for the Hartree-Fock approximation. It is clear that generally the asymptotic behavior does not differ too drastically from that of the Hartree-Fock scheme, in spite of the fact that for some states there are a substantial number of configurations which must be included. The largest change is for the $2s^2 2p\ {}^2P - 2s2p^2\ {}^2S$ transition where f_1 goes from 0.27 to 0.43, and this arises from the ground-state 2 × 2 configuration interaction,

TABLE V. Z-expansion perturbation energies (in a.u.) for a five-electron atom. V_1 is the first-order matrix element, which for the nondegenerate case is identical with the first-order energy ϵ_1.

Term	ϵ_0	V_1	ϵ_1
$2s^2 2p\ {}^2P$	−1.375	2.33445	2.32753
$2s2p^2\ {}^4P$	−1.375	2.38954	2.38954
$2s2p^2\ {}^2D$	−1.375	2.43994	2.43994
$2s2p^2\ {}^2S$	−1.375	2.47158	2.47158
$2s2p^2\ {}^2P$	−1.375	2.47744	2.47744
$2p^3\ {}^4S$	−1.375	2.52277	2.52277
$2p^3\ {}^2D$	−1.375	2.55441	2.55441
$2p^3\ {}^2P$	−1.375	2.57550	2.58242
$2s^2 3s\ {}^2S$	−1.30556	1.92496	1.91028
$2s^2 3p\ {}^2P$	−1.30556	1.96131	1.94548
$2s^2 3d\ {}^2D$	−1.30556	1.99265	1.98019

TABLE VI. The leading terms in the Z^{-1} perturbation expansion of the oscillator strength [Eq. (8)] for a five-electron atom.

Transition	Hartree-Fock		Exact	
	f_0	$\bar{f}_1$	f_0	$\bar{f}_1$
$2s^22p\ ^2P$-$2s2p^2\ ^2D$	0.0	1.050	0.0	0.850
$2s^22p\ ^2P$-$2s2p^2\ ^2S$	0.0	0.274	0.0	0.428
$2s^22p\ ^2P$-$2s2p^2\ ^2P$	0.0	2.570	0.0	2.042
$2s^22p\ ^2P$-$2s^23s\ ^2S$	0.014	• • •	0.016	• • •
$2s^22p\ ^2P$-$2s^23d\ ^2D$	0.696	• • •	0.700	• • •
$2s2p^2\ ^4P$-$2p^3\ ^4S$	0.0	0.799	0.0	0.799
$2s2p^2\ ^2D$-$2p^3\ ^2D$	0.0	1.030	0.0	1.030
$2s2p^2\ ^2D$-$2p^3\ ^2P$	0.0	0.407	0.0	0.636
$2s2p^2\ ^2P$-$2p^3\ ^2D$	0.0	1.154	0.0	1.154
$2s2p^2\ ^2P$-$2p^3\ ^2P$	0.0	0.883	0.0	1.404
$2s2p^2\ ^2S$-$2p^3\ ^2P$	0.0	1.247	0.0	1.006
$2s^23s\ ^2S$-$2s^23p\ ^2P$	0.0	3.926	0.0	3.016
$2s^23p\ ^2P$-$2s^23d\ ^2D$	0.0	1.410	0.0	1.236

$$2s^22p + 2p^3 \ .$$

Before going on to a description of the results for the isoelectronic sequence, it is pertinent here to briefly mention a refinement of this charge-expansion approach due to Cohen and Dalgarno,[18] which is designed to make the method yield quantitative results for at least a significant part of the sequence. In addition to the perturbation expansion of the total wave function, these authors also consider a Z expansion of the Hartree-Fock orbitals which they are able to calculate explicitly through first order. The asymptotic degeneracies and first-order Hartree-Fock corrections are combined to produce an explicit formula for the multiplet strength for the entire sequence. This very attractive approach thus leads to a charge-expansion approximation to the Hartree-Fock for those cases where there are no large-Z degeneracies, and, where there are, it predicts the modifications in the Hartree-Fock due to these configuration interactions.

IV. ISOELECTRONIC SEQUENCE *f* VALUES

With calculated f values spread out over three ions, (B I, C II, Ne VI) and the asymptotic behavior determined exactly, it should now be possible to draw in the f-value behavior fairly reliably in a plot of f versus Z^{-1}. This has been done here for all transitions for which calculations were done through $Z = 6$ (C II). Since some of the states of $2p^3$ are not bound for either B I or C II, although they are for Ne VI, transitions involving them are omitted from the present considerations. Furthermore, in view of the earlier discussion of the length and velocity forms, the following description will be restricted to the dipole-length form of the f value.

As an example of the kind of accuracy one can probably expect from such computational-graphical predictions, the $2s^22p\ ^2P$-$2s2p^2\ ^2D$ oscillator strengths are plotted in Fig. 1 and compared with the most recent measurements. It should be remarked that this transition is somewhat unusual in that it is the only one for which ac-

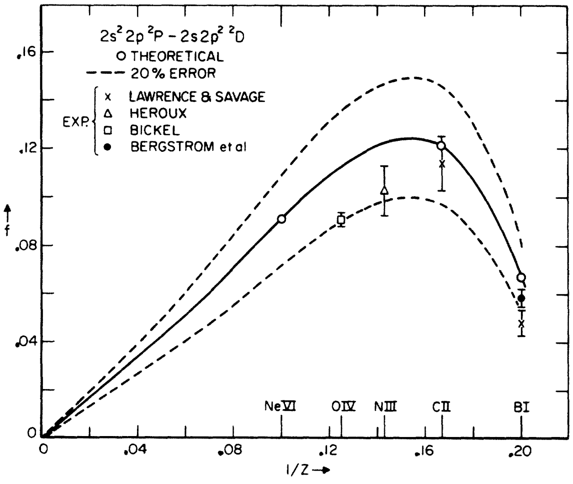

FIG. 1. Theoretical and experimental oscillator strengths versus Z^{-1} for the $2s^22p\ ^2P$-$2s2p^2\ ^2D$ transition in the boron isoelectronic sequence. The dashed curves correspond to hypothetical upper and lower error bounds of 20% on the theoretical curve. For the experimental values see Refs. 3–6.

curate experimental data is available for a number of the ions in the sequence (B I, C II, N III, O IV). No other transition is so blessed; indeed the rule is to find experimental data for only one or two ions, if any is available at all. In Fig. 1, a smooth curve has simply been drawn in free hand to connect the SOC calculated points, and the upper and lower limits are indicated for an assumed 20% uncertainty in the theoretical predictions. These error limits may be somewhat optimistic, since something in the neighborhood of 25% has been indicated as the kind of accuracy one can expect for this type of calculation. As Fig. 1 shows, 20% does encompass the measured values quite satisfactorily, with the theoretical curve being, if anything, slightly high.

This same transition is shown again in Fig. 2 where comparisons are now made with the predictions of both the charge-expansion method and the Hartree-Fock approximation. Several effects are evident here, which are important for understanding the behavior of the oscillator strength along the sequence. The Z-expansion curve indicates the effect of the ground-state configuration interaction

$$2s^22p + 2p^3,$$

which acts uniformly along the sequence to decrease the f value substantially from that of the single-configuration Hartree-Fock procedure. Both the SOC calculations and experimental determinations, however, show a marked bending over of the curve at the neutral end of the sequence. A detailed examination of the SOC wave function for the ^2D state of B I shows that configurations of the type $2s^2nd$ are quite important, and that they are responsible for a large cancellation in the transition moment. This then is an example of the redistribution of oscillator strength due to the perturbation of the $2s^2nd$ series by $2s2p^2$. In this case the perturber loses most of its oscillator strength to the series.[19] As the nuclear charge increases, the $2s2p^2$ energy level rapidly draws away from $2s^23d$ and the higher series members, so that this effect should die out for the higher stages of ionization with the f value approaching the charge-expansion curve, and this in fact is what appears to be happening.

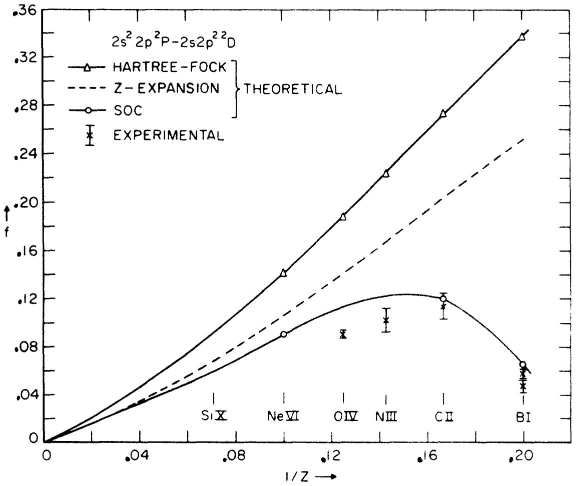

FIG. 2. f values versus Z^{-1} for the $2s^22p\ ^2P$-$2s2p^2\ ^2D$ transition in the boron sequence: a comparison of the present calculations (SOC) with Hartree-Fock, charge expansion, and experiment (same references as in Fig. 1).

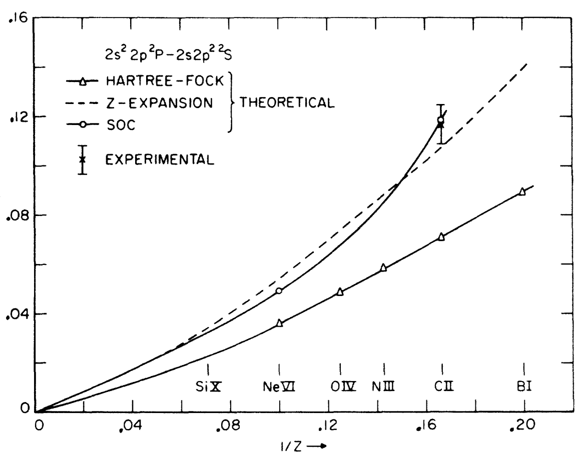

FIG. 3. f values versus Z^{-1} for the $2s^22p\ ^2P$-$2s2p\ ^2S$ transition in the boron sequence: a comparison of the Hartree-Fock and charge-expansion methods, and experiment (Ref. 4).

Another transition of interest is $2s^22p\ ^2P$-$2s2p^2\ ^2S$, which is shown in Fig. 3. Here the dominant effect appears to be the configuration interaction in the ground state, and the elaborate SOC calculation, in effect, confirms the predictions of the charge-expansion method. There appears to be a small enhancement of the f value at C II, where there is also good agreement with the lone experimental value.[4] The f value for boron was not calculated because of technical difficulties arising from the fact that $2s2p^2$ is here imbedded in the $2s^2ns$ series, with five series members below it. At C II, however, $2s2p^2$ is the lowest ^2S state, and it rapidly drops below $2s^23s$ for the higher stages of ionization. There is thus a level crossing in the neighborhood of C II, and, as pointed out by Zare[20] in a study of the magnesium sequence, such crossings can have a drastic effect on the oscillator strengths. While the SOC wave function for C II does contain a significant admixture of $2s^23s$, this does not appear to have affected the f values significantly, and it is of some interest to look at transitions from the ground state to the $2s^23s$ term.

The f values for this transition are shown in Fig. 4,[21] where the level-crossing configuration interaction shows up quite dramatically. The interference between $2s2p^2$ and $2s^23s$ is almost complete for C II which is closest to the crossing. The two experimental points tend to confirm, or at least do not contradict this theoretical curve. It should be remarked that an examination of the transition moment itself, i.e., the square root of the multiplet strength $S^{1/2}$, shows that in this case the minimum does not occur because of a change in the sign of $S^{1/2}$ along the sequence[22]; it maintains the same sign, simply becoming small at $Z = 6$. The wave function itself is predominantly $2s^23s$ for both B I and Ne VI (the coefficients are 0.954 and 0.962, respectively), with only small admixture of $2s2p^2$ (0.080 and 0.040, respectively). For C II, however, the mixing is rather strong, with $2s^23s$ and $2s2p^2$ coefficients of 0.889 and 0.358, respectively.

In Fig. 5, we show a transition where the dominant correlation correction appears to come from the asymptotic configuration interaction in the ground state and has a uniform effect along the entire sequence. Both the SOC and Z-expansion curves agree beautifully among themselves and with the experimental point for N III. The measurement on C II seems to indicate a turning down of the curve at the neutral end of the sequence, which is just the opposite of the theoretical predictions. While it is somewhat difficult to find a mechanism to account for such a behavior, it should be noted that since the discrepancy is not large ($\simeq$ 25%) it may not really be very significant.

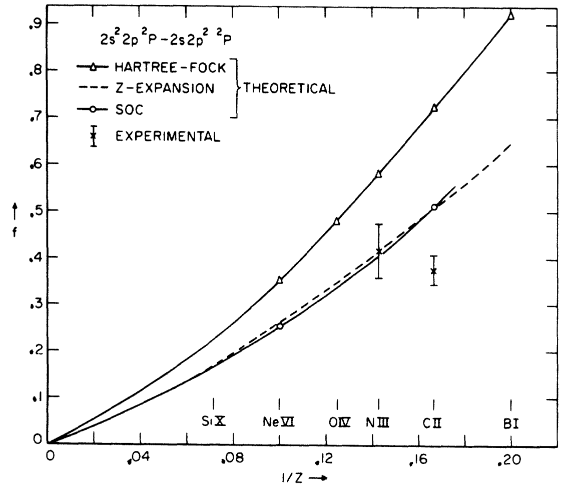

FIG. 5. f values versus Z^{-1} for the $2s^22p\,^2P$-$2s2p^2\,^2P$ transition in the boron sequence: comparison with Hartree-Fock, charge expansion, and experiment (Ref. 4).

Figure 6, finally, shows an example of a transition, $2s2p^2\,^2P$ - $2p^3\,^2D$, where neither state has any asymptotic configuration interaction. The charge-expansion and Hartree-Fock curves agree beautifully, as they should, and they both appear to give the wrong behavior. The lone experimental point here, an emission measurement of C II,[23] seems to support the trend predicted by the present SOC calculations, although there is a suggestion that they may be somewhat low. An analysis of the C II calculations shows that configurations of the type, $2s2p3d$, mix rather strongly into the $2p^3\,^2D$ state. The resulting cancellation thus provides a plausible

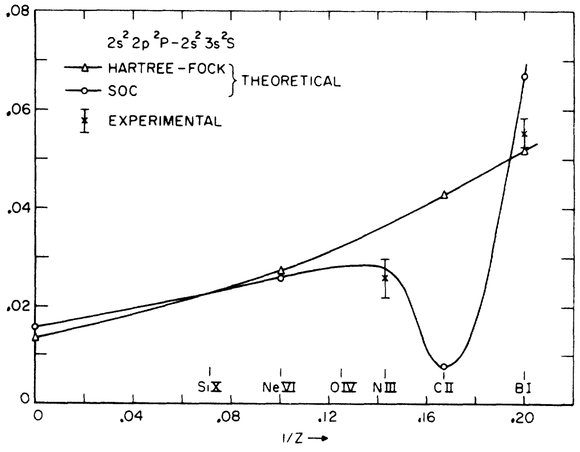

FIG. 4. f values versus Z^{-1} for the $2s^22p\,^2P$-$2s^23s\,^2S$ transition in the boron sequence: a comparison with Hartree-Fock and experiment (Refs. 4 and 6).

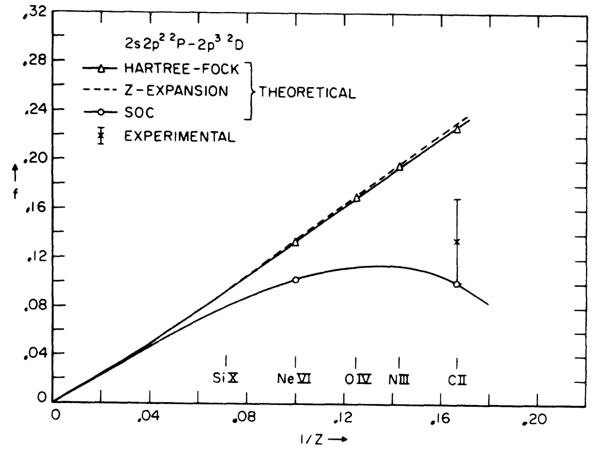

FIG. 6. f values versus Z^{-1} for the $2s2p^2\,^2P$-$2p^3\,^2D$ transition in the boron sequence: comparison with Hartree-Fock, charge expansion, and experiment (Ref. 23).

mechanism, in this case, for the C II f value being somewhat smaller than the Hartree-Fock. The $2s2p3d$ terms are just becoming bound at $Z = 6$ and are still quite close to $2p^3$. For higher stages of ionization, these two states pull apart, giving less mixing (for Ne VI); hence a diminishing effect on the oscillator strength. Some bending over of the f-value curve near the neutral end is thus probably real.

Similar plots have been made for the other transitions in the sequence; however, since there appears to be little more to be learned from them, there is no point in showing them here. For instance, the $2s2p^2\ {}^2D - 2p^3\ {}^2D$ f values behave much like the curves in Fig. 6, with the Z-expansion curve agreeing with the Hartree-Fock while the SOC one bends over at the neutral end, and for the same reasons. There is no experimental data for this transition. Also, the $2s2p^2\ {}^4P - 2p^3\ {}^4S$ curves look much like those of Fig. 5 for $2s^22p\ {}^2P - 2s2p^2\ {}^2P$, only with the Z expansion agreeing with the Hartree-Fock and the correlation corrections of the SOC serving to shift the f values uniformly down. The one very recent measurement here supports the SOC calculations.

The final results for the isoelectronic sequence are summarized in Table VII, where f values are given for each ion of the sequence through $Z = 15$. For the most part, these values have been obtained by fitting a truncated version of Eq. (8) to the SOC (dipole-length) data. In some of the more pathological cases, such as represented by Fig. 4, they have simply been read off of the graphs.

Assessing the accuracy of such theoretical data is always somewhat tricky. However, as discussed earlier, both internal consistency checks (agreement of length and velocity forms, convergence of SOC results) and comparisons with available experimental data strongly suggest something like 25% as a reasonable uncertainty, and this is provisionally recommended for all the data in Table VII. It is to be expected, of course, that intermediate-coupling effects will become important for the higher stages of ionization. Unfortunately, it is outside the scope of this paper to consider where and to what extent such departures from LS coupling will seriously affect these predictions. When this does happen, this data should at least provide an accurate starting point for an intermediate-coupling transformation.

V. SUMMARY

This paper has presented a study of the behavior of the oscillator strengths for a number of correlation-sensitive transitions along the boron isoelectronic sequence. This has been done by calculating the f value for a selection of ions in the sequence (B I, C II, Ne VI) and plotting these against the reciprocal nuclear charge Z, which is the natural independent variable. The f values were calculated with correlated wave functions by the method of superposition of configurations, and using the pseudonatural orbital technique to accelerate convergence. A variety of checks and comparisons indicates that this method is generally capable of achieving f-value accuracies in the 25% range. In order to also have the limiting large-Z behavior of these oscillator strengths, the necessary calculations were made in lowest order for the perturbation expansion in powers of Z^{-1}.

Graphs were drawn of the f value versus Z^{-1} for all these transitions and a substantial number of them were displayed and discussed. There were several points of interest here. One was the comparison of the calculations and graphical predictions with experimental data. Whenever such comparisons could be made, the agreement between these curves and the experimental points generally was good. The other point of interest centered around an intercomparison of the curves for the Hartree-Fock method, the Cohen-Dalgarno version of the charge-expansion method, and the present SOC calculations. Since these methods represent, roughly at least, successively more sophisticated approximations, such comparisons lay bare the theoretical mechanisms in many cases for the particular dependences of f values on nuclear charge. The asymptotic configuration interaction included in the charge-expansion method can strongly alter the f-value behavior from that of the Hartree-Fock, and often this is indeed the dominant correlation correction. When, however, the spectrum indicates that additional configuration interactions may be important, such as potential series perturbations or nearby level crossings, then one can have strong perturbations of the f values, resulting in a gross departure from the charge-expansion curve. In general, of course, the charge-expansion method leads to the correct f-value dependence for large enough Z, and the present study suggests this to be in the neighborhood of the fifth or sixth stage of ionization.

These theoretical curves have also been used to predict f values for the individual ions of this sequence through $Z = 15$ (P XI). While all indications point toward an expected accuracy of about 25%, further high-precision experimental confirmation is, of course, desirable.

APPENDIX

The coefficients of the ground-state wave functions for neutral boron and Ne VI are given in this appendix (Table VIII) to illustrate the types of configurations which enter into such calculations. Aside from the $2s$- and $2p$-functions, all the orbitals here are the PSNO's and bear little resemblance to spectroscopic orbitals (see Ref. 9). The signs of the coefficients are somewhat arbitrary,

TABLE VII. Theoretical oscillator strengths for the boron isoelectronic sequence through $Z=15$. The values for B I, C II, and Ne VI are directly calculated (dipole length) from SOC wave functions; the remainder are interpolated, either graphically or by fitting the *f*-value formula [Eq. (8)] to the calculation. Experimental data, where available is given in parentheses.[a]

$Z \to$ Transition	5	6	7	8	9	10	11	12	13	14	15
	0.067	0.121	0.123	0.113	0.102	0.091	0.082	0.074	0.067	0.062	0.057
$2s^22p\ ^2P$–$2s2p^2\ ^2D$	(0.048, 0.059)	(0.114)	(0.103)	(0.091)							
		0.119	0.089	0.071	0.058	0.050	0.044	0.039	0.035	0.032	0.030
$2s^22p\ ^2P$–$2s2p^2\ ^2S$		(0.118)									
		0.510	0.408	0.340	0.291	0.254	0.226	0.203	0.184	0.169	0.156
$2s^22p\ ^2P$–$2s2p^2\ ^2P$		(0.380)	(0.416)								
	0.067	0.008	0.028	0.028	0.027	0.026	0.025	0.024	0.024	0.023	0.022
$2s^22p\ ^2P$–$2s^23s\ ^2S$	(0.055)		(0.026)								
	0.197	0.330	0.422	0.486	0.533	0.567	0.593	0.613	0.629	0.641	0.651
$2s^22p\ ^2P$–$2s^23d\ ^2D$	(0.175)		(0.350)								
$2s2p^2\ ^2D$–$2p^3\ ^2D$		0.138	0.137	0.129	0.120	0.111	0.103	0.095	0.088	0.082	
		0.101	0.113	0.113	0.109	0.103	0.097	0.091	0.086	0.081	0.075
$2s2p^2\ ^2P$–$2p^3\ ^2D$		(0.136)									
	1.199	0.702	0.618	0.536	0.468	0.416	0.365	0.330	0.295	0.270	0.248
$2s^23s\ ^2S$–$2s^23p\ ^2P$											
	0.786	0.568	0.419	0.319	0.251	0.203	0.169	0.143	0.124	0.109	0.097
$2s^23p\ ^2P$–$2s^23d\ ^2D$											
	0.213	0.175	0.146	0.125	0.109	0.096	0.086	0.078	0.071	0.065	0.060
$2s2p^2\ ^4P$–$2p^3\ ^4S$		(0.168)									

[a] For B I, the experimental data are from Lawrence and Savage (Ref. 3) and Bergström *et al.* (Ref. 6). For C II, the data are from Heroux (Ref. 4), with the exception of the $2s2p^2\ ^2P$–$2p^3\ ^2D$ transition (Roberts and Eckerle, Ref. 23) and the $2s^22p\ ^2P$–$2s2p^2\ ^2D$ (Lawrence and Savage, Ref. 3). The N III data are from Heroux (Ref. 4) and O IV from Bickel (Ref. 5).

TABLE VIII. The ^2P ground-state SOC wave functions for neutral boron and Ne VI.

	Configurations	Coefficients	
		B I	Ne VI
1	$2s^22p$	0.9640	0.9801
2	$2p^3$	0.2029	0.1856
3	$(3s^2\,{}^1S)2p$	−0.0348	−0.0111
4	$(3p^2\,{}^1S)2p$	−0.0184	−0.0036
5	$(3d^2\,{}^1S)2p$	−0.0303	−0.0143
6	$(3s2p\,{}^1P)2s$	−0.0081	−0.0081
7	$(3s3p\,{}^1P)2s$	0.0461	0.0131
8	$(2p3d\,{}^1P)2s$	0.1206	0.0575
9	$(3p3d\,{}^1P)2s$	−0.0204	
10	$(3s2p\,{}^3P)2s$	0.0223	0.0099
11	$(3s3p\,{}^3P)2s$	0.0395	0.0117
12	$(2p3d\,{}^3P)2s$	0.0494	0.0243
13	$(3p3d\,{}^3P)2p$	−0.0108	
14	$(3p^2\,{}^3P)2p$	−0.0121	−0.0032
15	$(3p^2\,{}^1D)2p$	0.0116	0.0032
16	$(2p^2\,{}^3P)3p$	−0.0447	0.0016
17	$(2p^2\,{}^1D)3p$	0.0360	
18	$2p^2\,4f$	0.0112	0.0034
19	$(4s^2\,{}^1S)2p$	−0.0028	
20	$(4d^2\,{}^1S)2p$	−0.0066	−0.0021
21	$(4f^2\,{}^1S)2p$	−0.0086	−0.0044
22	$(3s4p\,{}^1P)2s$	−0.0050	
23	$(4s4p\,{}^1P)2s$	0.0028	0.0016
24	$(4p3d\,{}^1P)2s$	−0.0121	−0.0049
25	$(2p4d\,{}^1P)2s$	0.0030	
26	$(3p4d\,{}^1P)2s$	−0.0100	−0.0043
27	$(3d4f\,{}^1P)2s$	0.0174	0.0095
28	$(4d4f\,{}^1P)2s$	0.0039	
29	$(3s4p\,{}^3P)2s$	−0.0054	−0.0043
30	$(4s4p\,{}^3P)2s$	0.0028	
31	$(4p3d\,{}^3P)2s$	−0.0067	−0.0038
32	$(3p4d\,{}^3P)2s$	−0.0057	−0.0015
33	$(3d4f\,{}^3P)2s$	0.0106	0.0049
34	$(2p^2\,{}^3P)4p$	−0.0197	−0.0080
35	$(2p^2\,{}^1D)4p$	0.0148	0.0062

depending on the phase conventions used in defining the configurations, and the ones given here are just as they came off the computer. The important point, of course, is the magnitude of the coefficients; further details can be obtained by communicating directly with the author.

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Stark Effect in Hydrogenic Atoms: Comparison of Fourth-Order Perturbation Theory with WKB Approximation

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The Schrödinger equation for a hydrogenic atom in a uniform electric field is separated in parabolic coordinates, and WKB quantization rules are obtained for two of the separated equations. In the weak-field limit, the quantization rules are expanded in powers of the field and evaluated analytically. From the results, a power series for the energy eigenvalues is obtained which agrees with all known results of perturbation theory to fourth order. For strong fields, the quantization rules are evaluated numerically for states for which the perturbation series is expected to be least accurate. It is found that the perturbation results to fourth order agree with the numerical results for the energy eigenvalues to one part in a thousand for the highest fields possible, and that the addition of the fourth order in perturbation theory improves the accuracy of the perturbation series, contrary to the conclusions of an earlier work. Finally, the accuracy for the measurement of fields from observed Stark shifts by using the perturbation theory is estimated.

I. INTRODUCTION

The Stark effect in hydrogen has often been studied by perturbation theory. The first-order effect was derived by Schrödinger,[1] the second-order by Epstein,[2] the third-order by Doi,[3] and the fourth-order by Basu.[4] In practice, particularly in the measurement of electric fields from the observed Stark shifts, the energy eigenvalues must be known for high fields for which the application of perturbation theory is not *a priori* justified. Instead we apply the WKB method, which does not assume weak fields as perturbation theory does, to the Stark effect in hydrogenic atoms.

The most systematic derivation of the WKB quantization rule has been given by Dunham.[5] In his treatment, the eigenfunction of the one-dimensional Schrödinger equation,

$$-\frac{\hbar^2}{2m}\left(\frac{d^2\psi}{dx^2}\right) + V(x)\psi = E\psi, \tag{1}$$

is written

$$\psi(x) = \exp\left(\frac{i}{\hbar}\int^x y(x')dx'\right) . \tag{2}$$

The equation determining $y(x)$ is

$$\frac{\hbar}{i}\left(\frac{dy}{dx}\right) + y^2 = 2m(E - V), \tag{3}$$

which is solved by the WKB (asymptotic) expansion

$$y = \sum_{n=0} \left(\frac{\hbar}{i}\right)^n y_n(x) . \tag{4}$$