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Variational predictions of transition energies and electron affinities: He and Li ground states and Li, Be, and Mg core-excited states

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Variational procedures for predicting energy differences of many-electron systems are investigated. Several different calculations for few-electron systems are considered that illustrate the problems encountered when a many-electron system is modeled as a core plus outer electrons. It is shown that sequences of increasingly more accurate calculations for outer correlation may converge yielding wrong transition energies. At the same time, accurate core-polarization calculations overestimate the binding energy, requiring a core-valence correction. For the high-spin, core-excited states of Li, it was found that outer correlation only predicted electron affinities as accurately as full-correlation studies. This observation suggested a prediction of the core-excited ^4P-^4S transition in Be$^-$, based on observed $^3P^0$-^3P transition energies of the neutral species, predicted electron affinities including only outer correlation, and a core-valence correction, that is shown to be in good agreement with experiment. A similar calculation for Mg$^-$ predicts a wavelength of 2895.1 Å for this transition.

I. INTRODUCTION

In atomic spectroscopy, many properties depend on energy differences. Examples include transition energies, ionization potentials, and electron affinities. In many-electron systems, these properties can be predicted *approximately* by simple one-electron models. For example, in the Hartree-Fock model a self-consistent-field (SCF) potential is defined that determines the binding of a single electron in a many-electron system. Differences of such binding energies determine transition energies. In this model, the number of electrons in the system does not affect the complexity of the problem significantly. When accurate predictions are attempted, which take into account the correlation in the motion of the electrons, the situation changes. Variational calculations can deal efficiently with correlation between two electrons, and possibly more. The general model is one of a *core* plus *outer* electrons, where correlation among the outer electrons can be dealt with readily, but where correlation *with* the core may present difficulty, and hopefully correlation *in* the core can be neglected.

Using many-body perturbation theory (MBPT), given a complete basis of radial functions (or occupied and virtual orbitals), it is possible to develop expressions for energy differences, order by order, in which certain contributions in the energy difference cancel exactly and therefore can be omitted in the computational procedure. An example is the expression for the second-order binding energy of the outer electron in the alkali metals as given by Johnson, Saperstein, and Idrees.[1]

Many-body perturbation theory often relies on the zeroth-order wave function being a Hartree-Fock wave function where the latter is a single Slater determinant. Thus zero order near degeneracy, as in the ground state of Be $2s^2\,^1S$, is not easily dealt with. Lindgren and Morrison[2] describe a one- and two-particle many-body approach based on a pair equation, which may be evaluated order by order. This pair approach has been applied to the study of a number of properties.[3,4]

Variational methods such as the multiconfiguration Hartree-Fock[5] (MCHF) method and its relativistic analog, the multiconfiguration Dirac-Fock method[6] (MCDF), are general in that they can be applied to any system, provided energy expressions can be defined in terms of radial functions and the resulting systems of coupled, nonlinear integro-differential equations can be solved. These equations are solved iteratively by the self-consistent field method. In this paper we explore procedures of increasing complexity for the prediction of energy differences. It will be shown that some types of calculations may "converge" to inaccurate results, that others may yield an indication of the accuracy which may provide valuable information in the absence of reliable error estimates.

II. HELIUM GROUND STATE

Calculations for the helium ground state illustrate the difficulties that need to be overcome in the configuration model of an atom. As suggested by Sinanoglu,[7] a many-electron problem may, to good approximation, be separated into a set of two-electron problems. For the helium ground state, the total wave function may be expressed in terms of radial pair functions $f_l(r_1,r_2)$ and spin-angular coupling functions coupling two electrons with orbital quantum numbers l so that

$$\Psi=\sum_l f_l(r_1,r_2)|l^2\,^1S\rangle \ . \tag{1}$$

The pair functions are solutions of systems of partial differential equations. A pair program of the coupled cluster type was developed by Mårtensson[8] and applied to the helium ground state. More recent results have been obtained by Salomonson and Öster.[9] Grid extrapolation is used to estimate errors due to finite difference approximations and l extrapolation for the truncation of the infinite series in Eq. (1).

The MCHF method takes advantage of the symmetry with respect to the interchange of the two coordinates of each radial pair function and represents the function in terms of a one-electron radial basis so that

$$f_l(r_1,r_2)=\sum_n a_{nl}P_{nl}(r_1)P_{nl}(r_2) , \tag{2}$$

leading to a "reduced form" for the wave function.[10] MCHF calculations for the helium ground state have been performed in the same manner as those reported by Mårtenssen-Pendrill.[3] The results are compared in Table I. In the MCHF method, an extrapolation on n needs to be performed as well as on l. Since such extrapolations are sensitive to the accuracy of the individual results, a smaller grid size was used, one with twice the usual number of points[11] for a total of about 225 points in the ln$r$ variable. Table I shows the largest value of n in the calculation and the corrected value as determined by extrapolation. The latter was based on the ratio of the energy differences as a function of n. Let $\Delta E_n^l=E_n^l-E_{n-1}^l$ and $r_n=\Delta E_n^l/\Delta E_{n-1}^l$. The ratio r_n is a slowly increasing function, and this was used as a test for the SCF convergence and accuracy. Since we expect the correction to be small, we assumed that r_n was constant for the remainder of the series leading to a geometric series for the correction. Note that this procedure will slightly underestimate the correction. The extrapolation on l was performed by interpolating the last three values of $\Delta E^l=E^l-E^{l-1}$ to the expression

$$a_0(l+\tfrac{1}{2})^{-4}+a_1(l+\tfrac{1}{2})^{-5}+a_2(l+\tfrac{1}{2})^{-6} , \tag{3}$$

based on Schwartz's $(l+\frac{1}{2})^{-4}$ law,[12] and summing this expression until the last contribution was less than 10^{-10}. Because of the slowly converging nature of the series, values of l up to 100 were required for an energy lower than $-2.903\,724$ a.u. This clarifies the difficulty of full-correlation studies for many-electron systems. Note that the MCHF extrapolation value is slightly more accurate than the pair-equation limit which overestimates the energy.

There is an extensive literature on the extrapolation of the helium ground-state energy. The formula derived by Schwartz omitted the odd-order terms of Eq. (3), but like others,[3,13] we have included this term in our empirical extrapolation. A general theory for the rates of convergence for the Rayleigh-Ritz variational method for atoms and molecules has been derived by Hill.[14] This theory, when applied to the helium ground state, leads to the prediction that

$$E^l-E=c_1(l+1)^{-3}+c_2(l+1)^{-4}+O(l^{-5}) ,$$

where c_1 and c_2 have been determined from *exact* Hylleraas-type wave functions. This simpler correction, applied to E^5 in Table I, overestimated the energy by 1.68×10^{-6} a.u., and is not quite as accurate as our extrapolated value. The semiempirical formula used here, has been surprisingly accurate.

III. GROUND STATE OF LITHIUM

The $1s^22s\ ^2S$ ground state of lithium consists of a helium-like core plus an extra $2s$ electron. All the problems associated with the helium ground-state problem will be present, but the prediction of the binding energy of the $2s$ electron should be a simpler problem.

Table II reports the results obtained from calculations that include more and more orbitals in the wave-function expansion, the parameter characterizing the calculation being n, the largest principal quantum number. Thus the first row is for calculations in which the wave-function expansion contains all configuration states that can be formed from $1s$, $2s$, and $2p$ orbitals. Such an expansion is an "active space" expansion. Any orthogonal transformation of orbitals with the same angular momenta transforms the expansion coefficients of the total wave function but does not change the energy. Hence a variational procedure for determining the radial functions does not have a unique solution. One possibility is to determine solutions for which the off-diagonal Lagrange multipliers

TABLE I. Total energies (in a.u.) are reported for a sequence of MCHF calculations for helium. Extrapolated values are compared with similar results obtained using pair functions.

			E (extrapolated)	
l	n	E (MCHF)	MCHF	Salomonson *et al.*[a]
0	12	−2.879 028 617	−2.879 028 732	−2.879 028 8
1	13	−2.900 515 903	−2.900 516 088	−2.900 516 2
2	14	−2.902 766 353	−2.902 766 775	−2.902 766 8
3	14	−2.903 320 252	−2.903 320 980	−2.903 321 1
4	14	−2.903 517 316	−2.903 518 464	−2.903 518 6
5	14	−2.903 603 854	−2.903 605 520	−2.903 605 8
⋮				
∞			−2.903 724 080	−2.903 724 8
Exact[b]			−2.903 724 35. . .	−2.903 724 35. . .

[a] Reference 9.

[b] Reference 12.

TABLE II. Total energies and energy differences (in a.u.) for a series of fully variational calculations for Li^+ $1s^2\,{}^1S$ and Li $1s^22s\,{}^2S$.

Basis	$\mathrm{Li}^+\ {}^1S$	$\mathrm{Li}\ {}^2S$	ΔE Variable Li^+	 Fixed Li^+
2	−7.272 607 565	−7.454 565 281	0.181 957 7	0.196 436 3
3	−7.277 527 301	−7.473 184 268	0.195 657 0	0.196 512 9
4	−7.278 858 005	−7.476 203 010	0.197 345 0	0.197 739 3
5	−7.279 357 471	−7.477 159 86	0.197 802 4	0.197 938 8
6	−7.279 585 453	−7.477 577 76	0.197 992 3	0.198 077 0
7	−7.279 703 984	−7.477 766 62	0.198 062 6	0.198 109 2
⋮				

are zero,[16] but experience has shown that stability for the SCF iteration is computationally more important than the omission of the calculation of off-diagonal Lagrange multipliers, that the best stability was obtained by "applying Brillouin's Theorem," or, equivalently, deleting those configuration states from the wave-function expansion that differed from a major component of the wave function by one electron without a change in the spin-angular coupling. Thus, it was desirable to generate the configuration states in a way that facilitates this goal. For configuration states such as $1s3s({}^{1,3}S)2s$, the application of Brillouin's theorem would delete the $1s3s({}^1S)2s$ configuration state since it differs from the major $1s^2({}^1S)2s$ component by exactly one electron without a change in coupling. For higher angular momenta, it was helpful to see which was the largest component in the previous calculation before deciding on the configuration state to which Brillouin's Theorem should be applied. Generally, for this case, the $nln'l({}^1S)2s$ configuration states were removed, although at the $n=4$ stage the $1s2p({}^1P)4p$ configuration state became a large component and the $1s2p({}^1P)np$ configuration states were removed for $n=5,\ldots,7$. Once the radial functions had been determined, if convergence appeared difficult, a configuration-interaction (CI) calculation for an active space expansion was performed. In some cases, the energy was lowered, indicating the difficulty the multiconfiguration–self-consistent-field (MC-SCF) method had in achieving the rotation for a minimum energy.

Two types of energy differences are reported. The first is the difference of the two energies given in Table II obtained by optimizing the orbitals separately for each system. This was the scheme that had been used successfully in the calculations[17] for the binding of Ca^-. But it seems reasonable that the core energy should be computed using the same orbitals as the full system and this difference is tabulated in the last column. Indeed, the values in this column are more accurate. It is tempting to extrapolate the values, but a regular pattern has not been established to do so reliably. Our procedure combines the calculation of different singlet and triplet pair functions for which the asymptotic convergence rate is $[\frac{1}{2}(l+l')]^{-4}$ and $[\frac{1}{2}(l+l')]^{-6}$, respectively,[12] and includes not only the pair functions of a first-order wave function, which may explain the lack of an asymptotic pattern.

In MBPT, the binding energy of the alkalis can be expressed simply in terms of certain sums that do not require the calculation of correlation in the core. Such a procedure could aid a variational process as well, since the orbitals could then be optimized to represent the correlation of the outer electron with the core.

The simplest type of calculation is one which includes correlation with the core, also referred to as core polarization. In such a calculation, the configuration states that are included in the expansion are ones which can be obtained by single and double replacements from the reference configuration, or Hartree-Fock approximation, one of the orbitals being the valence orbital. In the Hartree-Fock approximation, the binding energy is always too small—correlation is needed to being results into agreement with observation. However, a core-polarization calculation, carried to convergence, will predict binding energies that are too large. This is seen in Table III. Thus we have a situation where a calculation may stop and be in excellent agreement with observation without being complete.

The reason for this overestimate is the neglect of core-valence interference. The presence of the valence electron reduces the correlation in the core. For example, the $1s^2\rightarrow 2s^2$ replacement is allowed in Li^+, but not in the $1s^22s$ ground state. The expression for $E^{(2)}$ given by Johnson, Saperstein, and Idrees[1] has some sums with a positive sign, whereas others are negative. These positive terms represent the core-valence interference, also referred to as an exclusion effect by Müller, Fleisch, and Meyer[18] in their study of intershell correlation effects.

In the next section of Table III, the orbitals from a core-polarization calculation are used in a full CI calculation, both for the three-electron system and the $1s^2\,{}^1S$ core. This difference now defines the binding energy. In this table, results are also compared with other theories and experiment. It should be noted that lithium is a light element and, in addition to a relativistic shift correction R, an elementary mass correction and a mass-polarization correction M need to be estimated and added to the non-relativistic NR energy before valid conclusions can be reached upon comparison with observation. The elementary mass correction is accounted for by using the Rydberg constant $\mathcal{R}_{\mathrm{Li}}=109\,728.727$ in converting from cm^{-1} to atomic units. MCHF calculations

TABLE III. Calculations for the binding energies (in a.u.) of $2s$ and $2p$ electrons in lithium. An integer i as a type of calculation implies that all configuration states are included in the expansion of the wave functions with orbitals whose principal quantum numbers are $n \leq i$. FCHF is a fixed-core Hartree-Fock calculation.

Type of calculation	$2s$	$2p$
(i) Core polarization only		
FCHF	0.196 321	0.128 673
3	0.198 455	0.130 054
4	0.198 748	0.130 229
5	0.198 816	0.130 337
(ii) With core-valence corrections		
3	0.197 761	0.130 120
4	0.198 047	0.130 231
5	0.198 102	0.130 246
(iii) With R+M	0.198 113	0.130 250
Pair theory[a] R	0.198 154	0.130 221
MBPT[b] R+M	0.198 158 4	0.130 235
Observed[c]	0.198 157 7	0.130 245 3

[a] Reference 20.
[b] Reference 21.
[c] Reference 22.

corrected for R are obtained by diagonalizing an interaction matrix in which the individual elements contain the J-independent Breit-Pauli corrections,[19] namely one- and two-body Darwin terms, mass-velocity correction, spin-spin contact, and mass polarization. The orbit-orbit (O-O) interactions are omitted. Similarly, for R+M calculations the matrix elements include the mass-polarization effects. Note that R includes a part of a Breit correction. Also, our procedure includes the effect of correlation on these quantities.

Results are compared with values reported by Lindgren[20] using nonrelativistic, coupled-cluster pair theory as well as some recent, highly accurate, and fully relativistic many-body perturbation theory results reported by Blundell *et al.*[21] The former appears to have used $\mathcal{R}_{\mathrm{Li}} = 109\,727.8$ in deriving the experimental values in a.u. and did not include the Breit and mass-polarization correction. For the $2s$ ionization energy a relativistic correction of 0.000 016 a.u. was used by Lindgren, which is the Dirac-Fock correction for the fixed-core Hartree-Fock ionization energy and is 0.000 005 a.u. larger than the present relativistic shift correction including the effect of correlation on the operators. The mass-polarization correction is small for the $2s$ but for the $2p$, the relativistic shift correction is negligible: the small discrepancy with observation in the present work arises when mass polarization is included. The MBPT results reported by Blundell *et al.* start from Dirac-Fock theory and add Breit and nuclear recoil effects. The latter includes the reduced mass correction. The experimental values reported in their paper are derived using R_∞ and so we have added the difference in our two experimental values to their reported value for present comparison purposes. In a variational calculation, the prediction of the binding of the $2p$ electron is more rapidly convergent than that of the $2s$. It is therefore surprising that this is not the case in these other theories.

Core-polarization calculations are easier to perform than fully variational calculations. The SCF iterations were stable with the application of Brillouin's theorem only to the $1s^22s$ or $1s^22p$ components. Since the $1s$ orbital was fixed, having been determined from a HF calculation for the $1s^22p$ state, the only deleted configurations were $1s^2ns$ and $1s^2np$ for the ^2S and ^2P states, respectively. When state-of-the-art results are not required, this approach is preferred, though an estimate of the core-valence interference should be included. An even simpler approach is the use of a core-polarization potential. A review of this approach is given by Müller, Fleish, and Meyer,[18] who also compare the results with *ab initio* configuration interaction calculations. In this approach, the core-valence correction, along with other corrections, are all treated as though they are part of core polarization.

IV. HIGH-SPIN, CORE-EXCITED STATES OF Li and Li$^-$

Optical studies of high-spin, multiply excited states of atoms have benefited from extensive interaction between theory and experiment. From a theoretical point of view, much can be learned about the importance of various physical effects, yet, when systems are small enough, theory has been able to make some accurate predictions. An example is Bunge's[23] prediction of a transition at 3489.8±0.8 Å in Li$^-$. Core-excited states also play an important role in continuum processes such as dielectric recombination. In fact, autoionization is an important factor in the lifetimes of such states.[24] Mannervik[25] has compiled an excellent review of both experimental and theoretical optical studies of multiply excited states.

In many theoretical studies the motivation has been the identification of observed lines, or even the prediction of lines. Here it must be remembered that the wavelengths of observed lines, if longer than 2000 Å, are reported in air, whereas theoretical energy differences, converted to wavelengths, predict wavelengths in vacuum. When highly accurate results are obtained it is important to apply Edlén's correction as described by Cowan.[26]

Table IV summarizes results from MCHF calculations for the $1s2s2p\;^4P^0$ and $1s2p^2\;^4P$ states of Li. Note that the outer correlation calculations have converged, but the transition wavelength is not correct. When core polarization was included, which is equivalent to a full-correlation study for this system, the p orbital was found to be very important and so, for each expansion, an extra p orbital was included. The notation $3,p$ is used to indicate a basis of all orbitals with $n \leq 3$ plus a $4p$ orbital. With such a basis, the transition energy is decreasing monotonically. An analysis of the contribution showed that, in the $5,p$ calculation, the $6p$ orbital was contributing slightly more in the $1s2p^2\;^4P$ state than in the $1s2s2p\;^4P^0$ state. Results are close to convergence. A geometric extrapolation, based on the ratio of the two

TABLE IV. Total energies (in a.u.), transition energies (in a.u.), and transition wavelengths (Å, in air) for different types of MCHF calculations for the $1s2s2p\ ^4P^0$ and $1s2p^2\ ^4P$ states of Li compared with those of other theories and observation. The notation i,p is used to indicate that all orbitals with $n \leq i$ are used in the expansion along with an extra p orbital.

Type of calculation	$E\ (^4P^0)$	$E\ (^4P)$	ΔE	λ (Å)
(i) Outer correlation only				
3	−5.365 040	−5.240 655	0.124 385	3678.2
4	−5.365 432	−5.241 174	0.124 257	3666.1
5	−5.365 498	−5.241 256	0.124 242	3666.5
(ii) With core polarization				
$3,p$	−5.366 561	−5.243 707	0.122 860	3707.8
$4,p$	−5.367 691	−5.245 007	0.122 684	3713.1
$5,p$	−5.367 917	−5.245 285	0.122 632	3714.7
Extrapolated			0.122 611	3715.3
(iii) With R+M			0.122 650	3714.1
With R+M+O-O			0.122 659	3713.9
Bunge and Bunge[a]				
NR	−5.367 948	−5.245 308	0.122 640	3714.4
Estimated NR	−5.367 992	−5.245 351	0.122 641	3714.4
Chung[b]				
NR	−5.367 870	−5.245 262	0.122 608	3715.4
R+M+O-O	−5.368 481	−5.245 823	0.122 658	3713.9
Observed[c]				3714

[a] Reference 29.

[b] Reference 27.

[c] Reference 28.

differences of ΔE, produces a value which, when corrected for relativistic effects (including orbit-orbit as reported by Chung[27]) and mass polarization, is in good agreement with experiment.[28] In this case, orbit-orbit interaction affects the wavelength to 0.27 Å. Thus it is negligible at the 1-Å level, but needs to be included when higher accuracy is desired.

It is interesting to compare these results with other theories. The total energies reported by Bunge and Bunge[29] are lower than the present ones, but as Chung

TABLE V. Total energies (in a.u.), transition energies (in a.u.), and transition wavelengths (Å, in air) for different types of MCHF calculations for the $1s2s2p^2\ ^5P$ and $1s2p^3\ ^5S$ states of Li^- are presented and compared with those of other theories and experiment. The notation i,sp is used to indicate that all orbitals with $n \leq i$ are used in the expansion of the wave function along with the one extra s and one extra p orbital.

Type	$E\ (^5P)$	$E\ (^5S^0)$	ΔE	λ (Å)
(i) Outer correlation only				
3	−5.381 345	−5.248 208	0.133 137	3421.6
4	−5.383 501	−5.251 379	0.132 132	3447.6
5	−5.383 820	−5.251 675	0.132 146	3447.2
(ii) Full correlation				
$3,sp;3,p$	−5.383 357	−5.251 602	0.131 755	3457.5
$4,sp;4,p$	−5.385 777	−5.255 043	0.130 734	3484.5
$5,sp;5,p$	−5.386 262	−5.255 777	0.130 485	3491.1
Extrapolated			0.130 405	3493.3
(iii) With R+M			0.130 453	3492.0
Bunge[a]	−5.386 346	−5.255 890	0.130 456	3491.9
With corrections				3489.8±0.9
Experiment[b]				3489.7±0.2

[a] Reference 23.

[b] Reference 30.

TABLE VI. Electron affinities (in a.u.) for core-excited states of Li as predicted by calculations for outer correlation only, and full correlation. The type of calculation was n for outer correlation, n,p for full correlation.

n	Outer	Full
	$1s2p^2$	
3	0.007 553	0.007 895
4	0.010 194	0.010 036
5	0.010 419	0.010 459
	$1s2s2p$	
3	0.016 305	0.016 284
4	0.018 069	0.018 000
5	0.018 322	0.018 308

pointed out, the agreement with observation was achieved without correcting for relativistic effects. Chung's total energies are slightly higher than the present values, but the NR and R+M+O-O values of the transition energies are in excellent agreement with the present values.

Similar calculations were performed for the $1s2s2p^2\,{}^5P$ and $1s2p^3\,{}^5S$ states of Li^- and these are summarized in Table V. In this case, it was found that in a $5,p$ calculation, the $5s$ orbital made a substantial contribution to the $1s2s2p^2\,{}^5P$ state and very little to the $1s2p^3\,{}^5S$ state, whereas the role of the $6p$ orbital, though not negligible, was more balanced. For this reason, calculations were performed with extra s and p orbitals for the ${}^5P$ state, and only an extra p in the ${}^5S$ state. Since this is now a four-electron system, wave-function expansions become lengthy and it was necessary to reduce the expansions by deleting all those configuration states whose coefficients were less than 0.000 05 in a first-order calculation where only the new orbitals were varied. The extrapolation process now leads to a much greater uncertainty.

V. PREDICTION OF ${}^5P$-${}^5S$ WAVELENGTH IN Be^- AND Mg^-

The energies reported in Tables IV and V permit a study of electron affinities as predicted by different procedures. Table VI shows that, for these core-excited states where the extra electron is a p electron, *outer-correlation studies predict the electron affinities as accurately as full-correlation studies.* The full-correlation electron affinities were obtained from basis sets of type n,p as indicated by the second column. The difference in electron affinities from outer correlation only is (0.008 752, 0.007 875, 0.007 903) for $n=3,4,5$, respectively. If we assume the difference has converged and use the last value as a correction to the observed energy difference[28] of 26 915.16 cm^{-1} for the $1s2s2p\,{}^4P-1s2p^2\,{}^4S$ transition in the neutral atom, the predicted wavelength for the $1s2s2p^2\,{}^5P-1s2p^3\,{}^4S$ transition in the negative ion is 3489.5 Å, in excellent agreement with experiment.

This procedure, if correct for other systems as well, would greatly simplify the prediction of wavelengths in more complex systems. For example, Gaarsted and Andersen[31] observed the $1s^22s2p\,{}^4P-1s^22p^3\,{}^4S$ transition at 2653.01±0.05 Å in Be^-, whereas Bunge's[32] full correlation studies, with some estimated corrections, predicted the wavelength to be 2645.0±3.0 Å. In effect, the experimental electron affinity for $1s^22p^2\,{}^3P$ was found to be 4.2 meV larger and not 10 meV smaller than the electron affinity for $1s^22s2p\,{}^3P$, as predicted by Bunge. Beck and Nicolaides[33] predicted a transition at 2654±9 Å.

Full-correlation studies for Be^- represents a considerable challenge for a variational procedure. Orbitals optimized for the total energy will tend to emphasize the core because of the larger correlation effects in this region, whereas the transition energy is largely an outer-electron property. As Tables III and IV have shown, the transition energy depends on correlation with the core as well as core-valence effects. By computing the electron

TABLE VII. Prediction of the ${}^4P-{}^4S$ transition of Be^- from outer correlation studies with corrections. $\mathcal{R}_{\text{Be}}=109\,730.628$ was used for conversion.

N	$EA\ (2s2p\,{}^3P)$	$EA\ (2p^2\,{}^3P)$	ΔEA	$\lambda\ ({}^4P$-${}^4S)$
(i) Outer correlation only				
3	0.008 761 1	0.008 153 2	0.006 079	2560.1
4	0.010 423 0	0.010 795 5	−0.000 372 5	2656.4
5	0.010 668 7	0.011 016 1	−0.000 347 4	2656.0
6	0.010 706 7	0.011 054 5	−0.000 347 9	2656.0
(ii) With core-valence correction			−0.000 181 0	2653.4
(iii) With R+M			−0.000 186 8	2653.2
Bunge[a]				2645.0±3.0
Beck and Nicolaides[b]				2654.0±9.0
Gaardsted and Andersen[c]				2653.01±0.05

[a] Reference 32.

[b] Reference 33.

[c] Reference 31.

TABLE VIII. Prediction of the ^4P-^4S transition of Mg$^-$ from outer correlation studies with corrections. $\mathcal{R}_{\text{Mg}}=109\,734.95$ was used for conversion.

N	EA ($3s3p\ ^3P$)	EA ($3p^2\ ^3P$)	ΔEA	λ (^4P-^4S)
(i) Outer correlation only				
3	0.007 365 1	0.013 864 9	−0.006 499 8	2894.7
4	0.013 530 6	0.019 902 8	−0.007 372 2	2910.8
5	0.013 956 1	0.020 277 8	−0.006 321 7	2891.2
(ii) With R+M				
	0.013 874 0	0.020 273 8	−0.006 399 8	2892.8
(iii) With $3s^23p^6$-valence interference			−0.006 522 2	2895.1
Beck[a]				2921

[a] Reference 34.

affinities for $1s^22s2p\ ^3P^0$ and $1s^22p^2\ ^3P$, including only outer correlation effects, and using the *observed* transition energy for the neutral atom, the core-polarization effects would be included along with some of the core-valence interference. But not all such interference. In the $^4P-^4S$ transition under consideration, in all cases except the $1s^22p^3\ ^4S$ state the $1s^2 \rightarrow 2p^2$ replacement is allowed. This correction must be included in the determination of a prediction of this transition energy based on the observed transition energy for $^3P^0-^3P$. This procedure is shown in Table VII for the $^4P-^4S$ transition of Be$^-$. The difference in electron affinities (EA) is indeed negative, as predicted by experiment.

Similar calculations have been performed for Mg$^-$ and are reported in Table VIII. Here the double replacements for the valence interference were restricted to the $2s^22p^6$ core of the major components of the wave function, namely, $3s3p^2$, $3s4p^2$, $3s3d^2$, $3p^23d$, $4s3p3d$, and $3p4p3d$ for the ^4P state and $3p^3$, $3p4p^2$, and $3p3d^2$ for the ^4S state. This value is significantly different from the value reported by Beck.[34]

It is interesting to compare these results with the recent values obtained by Beck. The calculations for the $3s3p^2\ ^4P$ state are the more difficult ones. Indeed, the outer-correlation study of Mg$^-$ consisted of a wave-function expansion of 172 configuration states for the $3s3p^2\ ^4P$ state compared with only 55 for the $3p^3\ ^4S$ state. Table IX presents a comparison of the two outer-correlation studies. The present total energies are consistently lower, though there is good agreement in the case of the neutral atom. The major difference arises in the calculation for the negative ion states where the present energies are lower, the largest difference being for the most difficult case.

TABLE IX. Comparison of MCHF results for Mg$^-$ and those reported by Beck (Ref. 34).

State	Beck	MCHF	Difference
E ($3s3p\ ^3P$)	−199.553 125	−199.553 200	0.000 075
E ($3s3p^2\ ^4P$)	−199.566 617	−199.567 156	0.000 539
EA ($3s3p\ ^3P$)	0.013 492	0.013 956	−0.000 464
E ($3p^2\ ^3P$)	−199.392 813	−199.392 820	0.000 007
E ($3p^3\ ^4S$)	−199.412 765	−199.412 993	0.000 228
EA ($3p^2\ ^3P$)	0.019 952	0.020 278	−0.000 326

VI. SUMMARY AND CONCLUSIONS

The variational method has been evaluated for a number of atomic systems. In the ground state of helium where highly accurate (well-converged) results could be obtained for each angular pair function, the data could be extrapolated and good accuracy achieved, though not of the same quality as the Pekeris[12] energies where the r_{12} interelectron distance is introduced explicitly into the wave-function expansion. For the $2s$ and $2p$ binding energies of Li, the simplest and most accurate calculations were core-polarization MCHF calculations, followed by full CI calculations for both Li and Li$^+$ core, to estimate the core-valence interference effect. The latter varied slightly with the size of the basis. Unlike the pair calculations for helium, the maximum principal quantum number n and orbital quantum number l both were increased by 1 in going from one stage to the next in a sequence of calculations. A disadvantage of this scheme is that the l extrapolations, as described for helium and similar to those used by Lindgren[20] and Blundell *et al.*,[21] could not be used. Such extrapolations are important for the $2s$ binding energy.

In the core-excited states of Li and Li$^-$ there is no correlation in the core, and core-polarization calculations do not need to be corrected for core-valence interference, though core polarization is crucial to the prediction of a transition energy. For Li, the transition energy from the sequence of calculations was so close to convergence that a geometric extrapolation produced results in excellent agreement with experiment. For Li$^-$, extrapolation is a larger correction and the agreement is not as good. The observation that core polarization was not important in the prediction of electron affinities for the core-excited states of Li, both states acquiring an extra p electron, suggested a scheme for predicting transition energies for the $^4P-^4S$ excited states of Be$^-$ and Mg$^-$.

Whenever a many-electron system can be modeled as *core* plus *outer* electrons, three types of correlation need to be considered: (i) outer correlation, (ii) correlation with the core, and (iii) correlation in the core. In many energy differences some of the latter two effects may cancel. The present calculations suggest that better accuracy is achieved when the MCHF variational procedure is applied to outer correlation, and the other effects estimated through CI calculations.

In many instances, the sequence of calculations terminated with the $n = 5$ basis (15 orbitals), largely because of code limitations. The full correlation studies of Li, where the ^2S selection rule kept the expansion from increasing too rapidly, exhibited convergence problems for the larger bases. More calculations with larger bases need to be tried, but better numerical accuracy, stability, and convergence rate for the MCHF-SCF procedure also would be desirable. No reasonable procedure for estimating the error resulted from this study.

At a high level of accuracy, many physical effects need to be included when comparing with observation. The present study was a nonrelativistic one, focusing on the correlation problem and correcting for relativistic effects in the Breit-Pauli approximation, in a manner which included the effect of correlation on these operators. Higher-order effects were not included, but the main conclusions about the variational process would also apply to MCDF calculation corrected for Breit and QED effects, along with nuclear recoil.

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