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Second-order energies and third-order matrix elements of alkali-metal atoms

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The recently introduced technique of constructing finite basis sets from *B*-splines for use in atomic-physics calculations is applied to the alkali-metal atoms Li, Na, K, Rb, and Cs. Valence energies are calculated within the framework of many-body perturbation theory to second order, and corrections to hyperfine splitting and transition matrix elements to third order in the approximation that a dominant subset of the terms in this order, associated with Brueckner orbitals, is evaluated. Agreement with experiment at the 1% level is found for all of the atoms considered. Comparisons are made with other calculations, and a short discussion of the systematic extension of this work is given.

I. INTRODUCTION

Recent experimental[1] and theoretical[2] interest in parity violation in heavy atoms has highlighted the general question of whether precision calculations of the properties of these complex systems are possible. The situation can be contrasted with that encountered in the simplest atom, hydrogen. There the apparatus of quantum electrodynamics (QED) leads to a systematic approach to calculating properties of the atom. The smallness of the fine-structure constant and the ratio of the electron mass to the proton mass make it possible to precisely define the amount of theoretical labor required to reach a given level of precision. If, for example, one needs a one part per million understanding of the fine structure of the atom, QED corrections to order α^3 and $\alpha^2 m_e/m_p$ must be evaluated, with higher-order contributions guaranteed (barring anomalously large coefficients) to be negligible at the order of interest. Such a situation would be desirable also for many-electron systems. While for the special case of helium, such a perturbation expansion has indeed been set up and successfully applied,[3] for atoms with more than two electrons the difficulty of directly solving for the many-electron wave function has inhibited progress in this direction. Several techniques are in current use to attack this problem, including multiconfiguration Hartree-Fock (MCHF),[4] configuration-interaction methods,[5] and many-body perturbation theory (MBPT).[6] There are two particularly attractive features that lead us to adopt MBPT for the present calculations. The first is that MBPT is directly related to a fundamental QED approach,[7] the use of a generalized Furry representation.[8] A similar approach has been recently advocated by Mohr[9] for the study of high-Z two-electron ions. The second is that the method is systematic, with well-defined levels of perturbation, so that one can hope to answer the kind of question posed above for hydrogen, viz., if it is desired to understand a property of a many-electron atom to, say, one tenth of a percent, how much theoretical labor and computer time will be required? Unfortunately, due to the complexity of MBPT and the difficulty of carrying out the related infinite sums over states, the answer to this question is not yet known. The purpose of this paper is to apply a recently developed numerical technique[10] at the level of second-order MBPT for ionization energies, and third order for transition matrix elements and hyperfine constants, to the alkali-metal atoms Li, Na, K, Rb, and Cs in order to investigate the nature of convergence in MBPT. Our results are encouraging at the 1% level: Starting from the Hartree-Fock model in lowest order, one finds a systematic improvement in agreement with experiment as one goes from lowest to third order. This makes it likely that the study of weak interaction effects in heavy atoms will be of value, since information accurate at the 1% level provides constraints on model building and the Weinberg angle competitive with those available from accelerator tests.[11] However, this level of precision is inadequate for tests of QED in neutral many-electron atoms, so that at least another order of perturbation theory must still be investigated. The plan of this paper is as follows. In Sec. II formulas from MBPT are quoted for second-order energies and third-order matrix elements, and justification for restricting our attention to a subset of the third-order matrix elements is presented. These terms are expressed in terms of products of radial integrals and angular momentum factors in Sec. III, where details of the calculation are given. Section IV contains a tabulation of our results, and in Sec. V, comparison is made with other calculations, and a discussion of the observed convergence of MBPT is given.

II. SECOND- AND THIRD-ORDER MBPT FORMULAS

Although the formalism of MBPT has been in place for several decades, explicit presentations of higher-order formulas have only rarely been given. A recent exception is the paper by Wilson,[12] which presents energy formulas up to fifth order for closed-shell systems. We have recently given[13] for a general potential formulas for second- and third-order energies and third-order matrix elements for systems with a single electron outside a closed shell. These lengthy formulas simplify considerably when the potential is taken to be the Hartree-Fock potential, defined by

$$(V_{\mathrm{HF}})_{ij}=\sum_{a}(g_{iaja}-g_{iaaj})\ , \qquad (1)$$

where

$$g_{abcd}=\int\frac{d^3x\,d^3y}{|\mathbf{x}-\mathbf{y}|}\psi_a^\dagger(\mathbf{x})\psi_c(\mathbf{x})\psi_b^\dagger(\mathbf{y})\psi_d(\mathbf{y}) \qquad (2)$$

are Coulomb integrals and where the summation includes all states a in the core. It is shown in Ref. 13 that the second-order corrections to the ionization energy of a valence electron v is for the Hartree-Fock potential

$$E^{(2)}=\sum_{n,a,b}\frac{g_{nvba}(g_{abnv}-g_{abvn})}{\epsilon_a+\epsilon_b-\epsilon_n-\epsilon_v}+\sum_{a,n,m}\frac{g_{avmn}(g_{mnav}-g_{mnva})}{\epsilon_a+\epsilon_v-\epsilon_n-\epsilon_m}\ , \qquad (3)$$

where the sums over n and m range over all positive energy states outside the core. As discussed in Ref. 7, a QED formulation also includes certain summations over negative energy states, but these terms are of order α^3 and can be neglected at the level of precision of interest here. The third-order matrix element is considerably more complicated: We present it in the form

$$Z^{(3)}=Z^{(3)}_{\mathrm{RPA}}+Z^{(3)}_{\mathrm{BO}}+Z^{(3)}_{\mathrm{SR}}+Z^{(3)}_{\mathrm{norm}}\ :$$

$$Z^{(3)}_{\mathrm{RPA}}=\sum_{a,b,n,m}\left[\frac{(g_{wnva}-g_{wnav})z_{bm}(g_{amnb}-g_{ambn})}{(\epsilon_m+\epsilon_w-\epsilon_b-\epsilon_v)(\epsilon_n+\epsilon_w-\epsilon_a-\epsilon_v)}+\mathrm{c.c.}\right]+\sum_{a,b,n,m}\left[\frac{(g_{mnab}-g_{mnba})z_{bm}(g_{awvn}-g_{awnv})}{(\epsilon_n+\epsilon_v-\epsilon_a-\epsilon_w)(\epsilon_m+\epsilon_w-\epsilon_b-\epsilon_v)}+\mathrm{c.c.}\right], \qquad (4a)$$

$$Z^{(3)}_{\mathrm{BO}}=\sum_{a,b,m,i}\left[\frac{g_{abmv}z_{wi}(g_{miba}-g_{miab})}{(\epsilon_i-\epsilon_v)(\epsilon_v+\epsilon_m-\epsilon_a-\epsilon_b)}+\mathrm{c.c.}\right]+\sum_{a,m,n,i}\left[\frac{g_{aimn}z_{wi}(g_{mnav}-g_{mnva})}{(\epsilon_i-\epsilon_v)(\epsilon_n+\epsilon_m-\epsilon_a-\epsilon_v)}+\mathrm{c.c.}\right], \qquad (4b)$$

$$\begin{aligned}Z^{(3)}_{\mathrm{SR}}=&\sum_{a,b,c,n}\left[\frac{g_{bavc}z_{cn}(g_{wnba}-g_{wnab})}{(\epsilon_n+\epsilon_w-\epsilon_c-\epsilon_v)(\epsilon_n+\epsilon_w-\epsilon_a-\epsilon_b)}+\mathrm{c.c.}\right]+\sum_{a,b,c,n}\frac{(g_{wnab}-g_{wnba})z_{ac}(g_{bcnv}-g_{bcvn})}{(\epsilon_n+\epsilon_v-\epsilon_b-\epsilon_c)(\epsilon_n+\epsilon_w-\epsilon_a-\epsilon_b)}\\&+\sum_{a,b,n,m}\left[\frac{(g_{mnav}-g_{mnva})z_{bm}(g_{awnb}-g_{awbn})}{(\epsilon_m+\epsilon_w-\epsilon_b-\epsilon_v)(\epsilon_n+\epsilon_m-\epsilon_a-\epsilon_v)}+\mathrm{c.c.}\right]+\sum_{a,b,n,m}\left[\frac{(g_{nwab}-g_{nwba})z_{bm}(g_{amvn}-g_{amnv})}{(\epsilon_m+\epsilon_w-\epsilon_b-\epsilon_v)(\epsilon_n+\epsilon_w-\epsilon_a-\epsilon_b)}+\mathrm{c.c.}\right]\\&+\sum_{a,b,m,n}\frac{g_{mnav}z_{ab}(g_{bwnm}-g_{bwmn})}{(\epsilon_n+\epsilon_m-\epsilon_b-\epsilon_w)(\epsilon_n+\epsilon_m-\epsilon_a-\epsilon_v)}+\sum_{a,b,m,n}\frac{g_{abvn}z_{nm}(g_{mwab}-g_{mwba})}{(\epsilon_n+\epsilon_v-\epsilon_a-\epsilon_b)(\epsilon_m+\epsilon_w-\epsilon_a-\epsilon_b)}\\&+\sum_{a,n,m,r}\left[\frac{g_{wrnm}z_{ar}(g_{mnav}-g_{mnva})}{(\epsilon_w+\epsilon_r-\epsilon_a-\epsilon_v)(\epsilon_n+\epsilon_m-\epsilon_a-\epsilon_v)}+\mathrm{c.c.}\right]+\sum_{a,n,m,r}\frac{(g_{awrn}-g_{awnr})z_{rm}(g_{mnav}-g_{mnva})}{(\epsilon_n+\epsilon_m-\epsilon_a-\epsilon_v)(\epsilon_r+\epsilon_n-\epsilon_a-\epsilon_w)}\ ,\end{aligned} \qquad (4c)$$

$$Z^{(3)}_{\mathrm{norm}}=\frac{1}{2}Z^{(1)}\left[\sum_{n,m,a}\frac{(g_{avnm}-g_{avmn})g_{nmva}}{(\epsilon_m+\epsilon_n-\epsilon_a-\epsilon_v)^2}+\sum_{n,a,b}\frac{(g_{abnv}-g_{abvn})g_{nvba}}{(\epsilon_v+\epsilon_n-\epsilon_a-\epsilon_b)^2}+\mathrm{c.c.}\right]. \qquad (4d)$$

In the above expressions v and w refer to two valence states (which are identical for discussion of hyperfine splitting), and the c.c. notation means that the previous term is to be complex conjugated and that the roles of v and w are to be interchanged. The sum over the index i in Eq. (4b) ranges over all states except for the valence state. The terms denoted by RPA are third-order random-phase approximation polarization corrections. These terms are grouped with lower-order terms in the present calculation, and evaluated as part of $Z^{(2)}$, the second-order matrix element.[14] In the following when second-order corrections are presented, they should be understood to include $Z^{(3)}_{\mathrm{RPA}}$ along with the infinite sum of higher-order RPA terms[15] necessary to ensure the equality of length and velocity forms for radial matrix elements. The terms denoted by BO, which stands for Brueckner orbitals,[16] are those that will be evaluated in this paper. These are clearly related to the second-order valence energy in Eq. (3), and are numerically dominant over the remaining terms in the sum. Had Brueckner orbitals been used in place of Hartree-Fock orbitals, these contributions would have been automatically accounted for in first order, just as the RPA terms are automatically accounted for in the second-order matrix element. The next group of terms are designated SR, for structural radiation, following the terminology of Ref. 17. As discussed in that paper, the SR terms are smaller than the BO terms because of their denominator structure. Specifically, a typical BO term has the denominator

$$(\epsilon_i-\epsilon_v)(\epsilon_n+\epsilon_m-\epsilon_a-\epsilon_v)\ ,$$

while a typical SR denominator is the following:

$$(\epsilon_w+\epsilon_r-\epsilon_a-\epsilon_v)(\epsilon_n+\epsilon_m-\epsilon_a-\epsilon_v)\ .$$

In an atom such as Cs, while $\epsilon_i - \epsilon_v$ can have a small value like 0.05 a.u. for $i = 6p$ and $v = 6s$, the smallest value that $\epsilon_w + \epsilon_r - \epsilon_a - \epsilon_v$ can have is $\epsilon_{6s} - \epsilon_{5p} = 0.28$. Therefore the denominator factors provide an automatic suppression factor of 0.18 between the BO terms and the SR terms. This factor is distinctly smaller for the lighter alkali metals, which is associated with the greater accuracy achieved in evaluating only the BO terms for the lighter systems considered here. These BO terms are considerably easier to compute than the numerous but smaller SR terms. Finally, the breakdown of the linked cluster expansion for open-shell systems[18] leads to the extra terms $Z^{(3)}_{\text{norm}}$, which are proportional to the first-order matrix element, the constant of proportionality being a derivative of the second order energy. As with the SR terms, the denominator structure tends to make these terms relatively small, and they will not be treated further in this paper.

III. REDUCTION TO RADIAL INTEGRALS AND METHOD OF CALCULATION

The completeness of the core allows the sums over magnetic substates in Eqs. (3) and (4) to be completed and the sums to be expressed in terms of radial integrals; this is one of the most important simplifying features of calculations involving alkali-metal atoms. After the angular momentum reduction, the Coulomb integral in Eq. (2) becomes proportional to the Slater integral

$$R_L(abcd) = \int dr\, dr' \frac{r_<^L}{r_>^{L+1}} [g_a(r) g_c(r) + f_a(r) f_c(r)] \times [g_b(r') g_d(r') + f_b(r') f_d(r')] \;, \tag{5}$$

where $g_a(r)$ and $f_a(r)$ are defined by

$$\psi_a(\mathbf{r}) = \frac{1}{r} \begin{pmatrix} g_a(r) & \Omega_{\kappa m}(\hat{\mathbf{r}}) \\ i f_a(r) & \Omega_{-\kappa m}(\hat{\mathbf{r}}) \end{pmatrix} , \tag{6}$$

the term $\Omega_{\kappa m}(\hat{\mathbf{r}})$ being a spherical spinor for the orbital a with angular momentum quantum numbers κ and m. In terms of Slater integrals the second-order energy given in Eq. (3) becomes

$$\begin{aligned} E^{(2)} = & -\sum_{a,n,m,L} \frac{C_L(vn)^2 C_L(am)^2}{[L][v]} \frac{R_L(vanm) R_L(nmva)}{\epsilon_n + \epsilon_m - \epsilon_a - \epsilon_v} \\ & - \sum_{a,n,m,L,L'} \frac{1}{[v]} C_L(vn) C_L(am) C_{L'}(vm) C_{L'}(an) (-1)^{L+L'} \begin{Bmatrix} v & n & L \\ a & m & L' \end{Bmatrix} \frac{R_L(vanm) R_{L'}(nmav)}{\epsilon_n + \epsilon_m - \epsilon_a - \epsilon_v} \\ & + \sum_{a,b,n,L} \frac{C_L(va)^2 C_L(nb)^2}{[L][v]} \frac{R_L(vnab) R_L(abvn)}{\epsilon_n + \epsilon_v - \epsilon_a - \epsilon_b} \\ & + \sum_{a,b,n,L,L'} \frac{1}{[v]} C_L(va) C_L(nb) C_{L'}(vb) C_{L'}(na) (-1)^{L+L'} \\ & \qquad \times \begin{Bmatrix} v & a & L \\ n & b & L' \end{Bmatrix} \frac{R_L(vnab) R_{L'}(abnv)}{\epsilon_n + \epsilon_v - \epsilon_a - \epsilon_b} \;, \end{aligned} \tag{7}$$

where

$$\begin{aligned} C_L(ab) & \equiv (-1)^{j_a + 1/2} [a]^{1/2} [b]^{1/2} \begin{pmatrix} j_a & j_b & L \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix} \pi(l_a, l_b, L) \\ \pi(l_a, l_b, L) & = \begin{cases} 1 & \text{if } l_a + l_b + L \text{ is even} \\ 0 & \text{if } l_a + l_b + L \text{ is odd} \end{cases} \end{aligned} \tag{8}$$

with $[a] \equiv 2j_a + 1$. It is entirely straightforward to evaluate Eq. (7) using a finite basis set approach: The only features requiring special care concern the choice of a grid for the B-splines and the truncation of the L sums. We define the B-splines on an exponential radial grid: Owing to limitations of computer time we presently restrict the grid to 50 points. As described in Ref. 10 our basis functions are chosen to satisfy boundary conditions in a finite cavity. The innermost point on the grid must be chosen small enough so that the small-r behavior of the wave functions is properly described, and the outermost point chosen large enough so that the low-lying excited states of the atoms that we are studying are not distorted by the finite radius of the cavity. In practice we have found that a maximum radius of 40 a.u. and an interior radius of 0.0001 a.u. gives results stable in the sense that further variation of these parameters leaves our results unchanged to three figures. Once the spline coefficients have been generated we recreate the wave function on a 400-point grid, and evaluate the Slater integrals needed to calculate $E^{(2)}$ using standard techniques. While the sum over the core states is performed exactly, the L summation is infinite, and must be approximated. We have chosen to cut off the summation at $L = 6$ and to accelerate the convergence of the sum with successive Aitken's extrapolations; again stability was found to three digits. Various other checks on the spline method, such as comparing the single excited state sum part of $E^{(2)}$ with the result obtained with standard differential equation techniques, and checking that finite nuclear size effects were corectly reproduced were performed, and satisfactory behavior was confirmed.

Turning now to the evaluation of matrix elements, it is seen that the evaluation of $Z_{\mathrm{BO}}^{(3)}$ is exactly parallel to that of the second-order energy, with one of the valence states replaced by a perturbed valence state. We illustrate this by considering the comparison of the third term in Eq. (4b) with the first term of Eq. (7) for the case of transition matrix elements. Carrying out the angular integrals leads to the contribution

$$\delta r_2 = \sum_{L,a,n,m,i} \frac{C_L(am)^2 C_L(nv)^2}{[L][v]} \times \frac{r_{wi} R_L(aimn) R_L(mnav)}{(\epsilon_i - \epsilon_v)(\epsilon_n + \epsilon_m - \epsilon_a - \epsilon_v)} , \tag{9}$$

where the angular quantum number associated with i is identical to that of v. By introducing a perturbed function $\overline{w}$ defined by

$$| \overline{w} \rangle \equiv \sum_i \frac{| i \rangle \langle i \, | \, r \, | \, w \rangle}{\epsilon_v - \epsilon_i} , \tag{10}$$

TABLE I. Ionization energies for valence states of the alkali metals calculated in second-order perturbation theory (atomic units).

State[a]	$E^{(0)}$	$E^{(2)}$	$E^{(0)}+E^{(2)}$	Expt.[b]
		Lithium		
$2s$	−0.196 32	−0.001 65	−0.197 97	−0.198 14
$2p^*$	−0.128 64	−0.001 37	−0.130 01	−0.130 24
$2p$	−0.128 64	−0.001 37	−0.130 01	−0.130 23
$3s$	−0.073 80	−0.000 35	−0.074 15	−0.074 18
$3p^*$	−0.056 77	−0.000 41	−0.057 18	−0.057 24
$3p$	−0.056 77	−0.000 41	−0.057 18	−0.057 24
$3d^*$	−0.055 56	−0.000 04	−0.055 60	−0.055 61
$3d$	−0.055 56	−0.000 04	−0.055 60	−0.055 61
		Sodium		
$3s$	−0.182 03	−0.005 88	−0.187 91	−0.188 86
$3p^*$	−0.109 49	−0.001 78	−0.111 27	−0.111 60
$3p$	−0.109 42	−0.001 77	−0.111 19	−0.111 52
$3d^*$	−0.055 67	−0.000 23	−0.055 90	−0.055 94
$3d$	−0.055 67	−0.000 23	−0.055 90	−0.055 94
$4s$	−0.070 16	−0.001 26	−0.071 42	−0.071 58
		Potassium		
$4s$	−0.147 49	−0.012 45	−0.159 94	−0.159 52
$4p^*$	−0.095 71	−0.004 62	−0.100 33	−0.100 35
$4p$	−0.095 50	−0.004 55	−0.100 05	−0.100 09
$3d^*$	−0.058 07	−0.002 76	−0.060 82	−0.061 39
$3d$	−0.058 08	−0.002 77	−0.060 84	−0.061 40
$5s$	−0.061 09	−0.002 86	−0.063 94	−0.063 71
		Rubidium		
$5s$	−0.139 29	−0.015 01	−0.154 30	−0.153 51
$5p^*$	−0.090 82	−0.005 44	−0.096 25	−0.096 19
$5p$	−0.089 99	−0.005 19	−0.095 18	−0.095 11
$4d^*$	−0.059 69	−0.004 78	−0.064 47	−0.065 32
$4d$	−0.059 74	−0.004 76	−0.064 50	−0.065 32
$6s$	−0.058 70	−0.003 46	−0.062 16	−0.061 77
		Cesium		
$6s$	−0.127 37	−0.017 74	−0.145 11	−0.143 10
$6p^*$	−0.085 62	−0.006 91	−0.092 53	−0.092 17
$6p$	−0.083 78	−0.00618	−0.089 97	−0.089 64
$5d^*$	−0.064 42	−0.011 16	−0.075 58	−0.077 04
$5d$	−0.064 53	−0.010 84	−0.075 37	−0.076 59
$7s$	−0.055 19	−0.004 20	−0.059 39	−0.058 65

[a] Notation: $p^* = p_{1/2}$, $p = p_{3/2}$, etc.
[b] Reference 19.

Eq. (9) can be written

$$\delta r_2 = -\sum_{L,a,n,m} \frac{C_L(vn)^2 C_L(am)^2}{[L][v]} \frac{R_L(\bar{w}anm) R_L(nmva)}{\epsilon_n+\epsilon_m-\epsilon_a-\epsilon_v} . \tag{11}$$

Since the perturbed orbital $|\bar{w}\rangle$ can be formed before any sums are performed, evaluation of these terms clearly involves little more computation than the energy calculations. In particular, all the angular momentum selection rules are unchanged. This simplicity will be lost once SR terms are considered, and their complete evaluation will require a different order of computational effort.

IV. TABULATION OF RESULTS

In this section the results of evaluating second-order energy corrections and third-order BO matrix elements are presented. While there are no first-order corrections to the zeroth-order Hartree-Fock energies, there are nontrivial second-order corrections for matrix elements. The method used to calculate these corrections is essentially identical to that used in Ref. 14. In Tables I—III below we summarize our results for ionization energies, hyperfine constants, and transition matrix elements, giving the contributions from the first few orders of perturbation theory and the sum of the theoretical contributions compared with experiment. We assign a theoretical uncertainty of 1 to the last digit of all second-order energy and third-order matrix element results: The lower-order terms are accurate to all digits displayed. It would be straightforward to reduce the theoretical error by several orders of magnitude by working with larger basis sets and more partial waves, but this is not yet necessary given the relatively large discrepancy between theory and experiment due to uncalculated higher-order terms.

V. DISCUSSION AND COMPARISON WITH OTHER CALCULATIONS

Before discussing the convergence of MBPT that can be inferred from the above tables, we compare our calculations with previous *ab initio* calculations, working from Li through Cs.

MBPT was first applied to the $2s$ ground state of lithium by Chang, Pu, and Das[36] and to the $2p$ excited state by Lyons, Pu, and Das.[37] Recently a rather complete MBPT study of lithium was made by Lindgren,[38] who

TABLE II. Hyperfine constants for valence states of the alkali metals calculated in third-order perturbation theory (units: MHz).

State[m]	$A^{(1)}$	$A^{(2)}$	$A^{(3)}$	Sum	Expt.
^{7}Li $I=\frac{3}{2}$ $g_I=2.17065$					
$2s$	284.34	105.53	10.00	399.87	401.75[a]
$2p^*$	32.29	11.61	2.01	45.91	46.17(35)[b]
$2p$	6.46	−10.57	0.40	−3.71	−3.07(13)[c]
^{23}Na $I=\frac{3}{2}$ $g_I=1.47749$					
$3s$	623.53	143.62	93.25	860.90	885.82[d]
$3p^*$	63.39	18.89	9.11	91.40	94.3(2)[e]
$3p$	12.59	5.41	1.80	19.80	18.65(10)[f]
$4s$	150.46	34.22	16.71	201.38	202(3)[g]
^{39}K $I=\frac{3}{2}$ $g_I=0.26064$					
$4s$	146.71	34.69	45.25	226.65	230.86[h]
$4p^*$	16.62	4.89	4.92	26.43	28.85(30)[i]
$4p$	3.23	2.15	0.95	6.33	6.09(4)[h]
^{85}Rb $I=\frac{5}{2}$ $g_I=0.541208$					
$5s$	643.9	135.8	233.5	1013.2	1011.9[j]
$6s$	172.0	35.9	37.4	245.3	239.2(1.2)[k]
^{133}Cs $I=\frac{7}{2}$ $g_I=0.7377208$					
$6s$	1435	289	642	2366	2298[l]
$7s$	394	80	98	572	546[k]

[a] Reference 20.
[b] Reference 21.
[c] Reference 22.
[d] Reference 23.
[e] Reference 24.
[f] Reference 25.
[g] Reference 26.
[h] Reference 27.
[i] Reference 28.
[j] Reference 29.
[k] Reference 30.
[l] Reference 31.
[m] Notation: $p^*=p_{1/2}$, $p=p_{3/2}$, etc.

TABLE III. Reduced matrix elements for the resonance transitions $ns \rightarrow np^*$, np in alkali-metal atoms calculated in third order (units: ea_0).

Transition[e]	$D^{(1)}$	$D^{(2)}$	$D^{(3)}$	Sum	Expt.
		Lithium			
$2s \rightarrow 2p^*$	3.364	−0.014	−0.029	3.321	3.305(1)[a]
$2s \rightarrow 2p$	−4.758	0.020	0.041	−4.697	−4.674(2)[a]
		Sodium			
$3s \rightarrow 3p^*$	3.691	−0.043	−0.102	3.545	3.513(1)[a]
$3s \rightarrow 3p$	−5.219	0.061	0.145	−5.013	−4.947(1)[a]
		Potassium			
$4s \rightarrow 4p^*$	4.555	−0.154	−0.314	4.087	4.08(8)[b]
$4s \rightarrow 4p$	−6.439	0.217	0.444	−5.778	−5.77(11)[b]
		Rubidium			
$5s \rightarrow 5p^*$	4.819	−0.213	−0.420	4.186	4.11(6)[c]
$5s \rightarrow 5p$	−6.802	0.296	0.600	−5.906	−5.90(7)[c]
		Cesium			
$6s \rightarrow 6p^*$	5.278	−0.303	−0.582	4.393	4.52(1)[d]
$6s \rightarrow 6p$	−7.426	0.413	0.842	−6.171	−6.36(1)[d]

[a] Reference 32.
[b] Reference 33.
[c] Reference 34.
[d] Reference 35.
[e] Notation: $p^* = p_{1/2}$, $p = p_{3/2}$, etc.

calculated energies and hyperfine constants using Brueckner orbitals, and who made extensive comparisons with older work. The present perturbation theoretic treatment of correlation is just the first step in an iterative scheme, which ultimately leads to the description in terms of Brueckner orbitals used in Ref. 38. Numerically our correlation corrections for the $2s$ and $2p$ ionization energies in Li,

$$E^{(2)}_{2s,2p} = -0.001\,649,\ -0.001\,375 \text{ a.u. },$$

agree very well with the values obtained after one iteration in Ref. 38, viz.,

$$\Delta E_{2s,2p} = -0.001\,637,\ -0.001\,360 \text{ a.u.}$$

The small differences are presumably due to the fact that only terms with $l \leq 4$ are included in first iteration in Ref. 38. It should be mentioned that the final values of the ionization energies obtained after the iteration scheme had converged, agreed with measurements to five significant figures. The values for our third-order corrections to the lithium hyperfine constants compare very well with corresponding values obtained by Lindgren[38] in the first iteration of the Brueckner orbital equations. Since no other higher-order MBPT calculations of transition amplitudes in lithium are available we compare our values of transition amplitudes with the calculations of Sims *et al.*,[39] who employed methods on Hylleraas coordinates to obtain

$$f(\text{Li},2s_{1/2} \rightarrow 2p_{1/2}) = \tfrac{1}{3}0.7476\ ,$$

(Ref. 39) for the oscillator strength. This value can be compared with the result

$$f(\text{Li},2s_{1/2} \rightarrow 2p_{1/2}) = \tfrac{1}{3}0.7495\ ,$$

from the present calculation. It is seen that the two theoretical results agree better with one another than with the measured value,[32]

$$f(\text{Li},2s_{1/2} \rightarrow 2p_{1/2}) = \tfrac{1}{3}0.7416(12).$$

For sodium there are no previously published MBPT calculations of ionization energies; however, one can obtain comparison values for correlation corrections to ionization energies from the MCHF calculations of Froese Fischer.[40] For the $3s$, $3p$, and $4s$ states the values of the correlation energies deduced from the MCHF calculations are the following:

$$E^{(2)}_{3s,3p,4s} = -0.006\,65,\ -0.002\,13,\ -0.001\,47 \text{ a.u. },$$

which agree approximately with the values,

$$E^{(2)}_{3s,3p,4s} = -0.005\,89,\ -0.001\,78,\ -0.001\,26 \text{ a.u.}$$

from the present perturbation theory calculations. Indeed, the MCHF wave functions used in the calculations of Ref. 40 included configurations with the valence electron and a single core electron excited; these are precisely the excitations appearing in Eq. (3). The transition amplitudes given in the present calculation also agree well with the results from Ref. 40. For the resonance transition $3s_{1/2} \rightarrow 3p_{1/2}$ one finds the following values for the first-, second-, and third-order contributions to the transition amplitude:

$$D^{(1,2,3)}=\begin{cases}3.691,\ -0.043,\ -0.102\ (\text{present})\\ 3.695,\ -0.046,\ -0.119\ (\text{Ref.}40)\ .\end{cases}$$

The resulting theoretical values

$$D_{\mathrm{MCHF}}(\mathrm{Na},3s_{1/2}\rightarrow 3p_{1/2})=3.530$$

from Ref. 40 and

$$D_{\mathrm{MBPT}}(\mathrm{Na},3s_{1/2}\rightarrow 3p_{1/2})=3.545$$

from the present calculation agree better with one another than with the measured value[32]

$$D_{\mathrm{expt}}(\mathrm{Na},3s_{1/2}\rightarrow 3p_{1/2})=3.513(1)\ .$$

We have also confirmed that the present values for the ionization energies of the $3s$ and $3p$ states of sodium as well as the value of the $3s$ hyperfine constant agree well with the first iteration of the corresponding Brueckner orbital calculation.[41] Many-body calculations of the Na $3s$ hyperfine constant were also carried out by Lee, Dutta, and Das[42] who obtain a value

$$A(\mathrm{Na},3s_{1/2})=857.80\ \mathrm{MHz}$$

compared to the present value

$$A(\mathrm{Na},3s_{1/2})=860.99\ \mathrm{MHz}\ .$$

Part of the difference in the two values is because relativistic corrections are included in the present calculations, another part because the complete core polarization corrections are included, and finally because summations over excited states are carried out more fully in the present work.

We were unable to find suitable comparison calculations for potassium except for the configuration-interaction (CI) calculation of Ref. 5. These CI calculations give values for energies, hyperfine constants, and transition amplitudes in very close agreement with experiment, but the polarization potential used involves an adjustable cutoff parameter. The comparison of the present calculations with these CI calculations is essentially identical to the comparison with experiment. Among the lower-order *ab initio* calculations we mention the systematic calculations of relativistic all-order polarization corrections to hyperfine constants[43] which gives excellent agreement with the present second-order hyperfine constant for the $4s$ state of K and for the ground states of the other alkali-metals as well.

For rubidium the present calculations of the ground-state hyperfine constant,

$$A(^{85}\mathrm{Rb},5s_{1/2})=1013.2\ \mathrm{MHz}$$

compares well with the value

$$A(^{85}\mathrm{Rb},5s_{1/2})=1020.7\ \mathrm{MHz}$$

from the relativistic many-body calculations of Vajed-Samii *et al.*[44]

For cesium extensive relativistic many-body calculations have been made of correlation corrections to ionization energies,[45] hyperfine constants,[46] and transition amplitudes,[47] by Dzuba *et al.* The present values for the second-order corrections to ionization energies should agree with the corresponding values from Ref. 45, since the two calculations are formally identical. We find, however, disagreements at the few percent level between the two calculations, that may possibly be due to the different number of partial waves considered. We have retained at all terms contributing to the sums with $l\leq 6$ in the present work and have made an attempt to estimate the remainder for $l>6$ using Aiken's method. In Table IV we compare values from the present calculation with perturbation theory values from Ref. 45, with Brueckner orbital values from Ref. 47, and with experiment. Values for the hyperfine constants for cesium from the present calculation compare favorably with the values in Ref. 46, which were obtained using somewhat different methods; we treat all excitation channels, but evaluate only the BO terms in $Z^{(3)}$, whereas Dzuba *et al.* include only l diagonal (and in the third-order matrix element only j diagonal) excitation channels but in this approximation evaluate all third-order contributions. We find

$$A(^{133}\mathrm{Cs})=\begin{cases}2366.4\ \mathrm{MHz}\\ 2346.5\ \mathrm{MHz}\end{cases}\ \text{for }6S_{1/2}\ ,$$

$$A(^{133}\mathrm{Cs})=\begin{cases}571.8\ \mathrm{MHz}\\ 561.5\ \mathrm{MHz}\end{cases}\ \text{for }7s_{1/2}\ ,$$

where the upper values are from the present calculation and the lower from Ref. 46. The correlation contributions from the two calculations agree with one another at the level of a few percent. The present calculations of

TABLE IV. Comparison of ionization energies for states of cesium from the present calculation with other theoretical and measured values (energies in a.u.).

State	HF	HF + corr[a]	BO[b]	Present	Measurement[c]
$6s_{1/2}$	−0.127 37	−0.143 25	−0.144 45	−0.145 11	−0.143 10
$6p_{1/2}$	−0.085 62	−0.092 14	−0.092 72	−0.092 53	−0.092 17
$6p_{3/2}$	−0.083 78	−0.089 61	−0.090 12	−0.089 97	−0.089 64
$5d_{3/2}$	−0.064 42	−0.074 64	−0.075 79	−0.075 58	−0.077 04
$5d_{5/2}$	−0.064 53	−0.074 35	−0.075 24	−0.075 37	−0.076 59
$7s_{1/2}$	−0.055 19	−0.058 89	−0.058 55	−0.059 39	−0.058 65

[a] Reference 45.

[b] Reference 47.

[c] Reference 19.

$6s \rightarrow 6p_{1/2}$ transition amplitudes for Cs can be compared with results from Ref. 47

$$D(6s_{1/2} \rightarrow 6p_{1/2}) = \begin{cases} 4.40 \text{ (present)} \\ 4.45 \text{ (Ref.47, length form)} \\ 4.52(1) \text{ (expt)} . \end{cases}$$

The method used in Ref. 46 is different from the present approach in that approximate Brueckner orbitals were evaluated, and these orbitals were used to determine the first- and second-order transition matrix elements. The agreement between the two approaches is seen to be satisfactory at the few percent level.

The most obvious feature of the Tables I—III is that an *ab initio* description of atomic properties valid at the few percent, and sometimes significantly better than 1% level is being achieved. It is also clear that without inclusion of the BO terms the agreement degenerates to about the 10% level. Therefore we are in a position to claim for the alkali-metal atoms that second-order energy calculations and a particular subset of third-order matrix element calculations suffice to make predictions accurate at the 1—2 % level for the heavier atoms, and 0.1—0.5 % for the lighter atoms. It is possible that similar accuracy may be achievable for other one-valence electron atoms, such as those of the boron period, but because the argument about the dominance of the BO terms breaks down for these atoms a full calculation including SR terms may be required.[17] It is also possible that the agreement found is fortuitous. However, given the large number of experimental observables all described accurately by this method, we consider this unlikely. We would consider further improvement in the agreement between theory and experiment in going to the next order of MBPT as convincing evidence that the perturbation theory is converging smoothly. While this extension would be an extremely large scale task, the increasing power of supercomputers means that it is not impossible. The results in this paper involved about five hours of computation on a Cray X-MP/24. We estimate that the SR terms, if carefully coded, could be done in about 15 hours. It is difficult to precisely estimate the amount of time for a complete evaluation of third-order energies and fourth-order matrix elements, but we expect that less than 200 h would be required. If indeed such calculations can be performed and accuracies of well under 1% achieved, then in addition to obtaining high precision information about the weak interactions from atomic physics, one would also begin to test QED in neutral many-electron atoms.

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