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Numerical study of the role of shielding and exchange effects and of correlation and relativistic corrections in the Dirac-Fock approximation

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The purpose of this work is to provide a quantitative underpinning to the qualitative understanding of the various physical effects which play a role in the spectra of many-electron atoms. Shielding and exchange contributions are studied, as functions of the principal quantum number n, the orbital angular momentum l, and the nuclear charge Z, for neutral alkali-metal atoms in the Dirac-Fock (DF) approximation. Fine-structure effects and valence-state correlation corrections to the DF approximation are also considered for these atoms. Breit interaction and correlation corrections are discussed for the core states of noble gases. Previous numerical computations of these various contributions to atomic energy levels by others are extended to provide a larger data set to serve as a basis for the study of estimates and trends.

I. INTRODUCTION

Our aim in this article is to provide a numerical basis for a qualitative understanding of the relative magnitudes of various physical effects which contribute to the bound-state energies of many-electron atoms. We will be dealing throughout with the Dirac-Fock (DF) approximation, and some corrections to it. Studies of electron shielding in the Hartree approximation are as old as the approximation itself, and serve as the basis for various model potentials,[1,2,3] which take that shielding into account. The relative importance of exchange contributions in the Hartree-Fock approximation has also been studied, and the contribution of the Breit interaction has been computed.[4] Correlation corrections to the (DF) energies have been recently calculated[5] as well.

Our present purpose is to bring the study of all these calculations under a single umbrella, and to cast a light on the relative importance of various contributions as one proceeds outward from the inner core of the atom to the valence states, or, alternatively, from linear to circular orbits for a given principal quantum number. Further, we propose to examine the dependence of these effects on the value of nuclear charge.

The system studied is that of the frozen core: Only the closed shells (or subshells) of core electrons are considered in the determination of the effective DF potential and wave functions. Valence-electron DF equations, when the corresponding eigenvalues are relevant to the study of various trends, are then solved in the frozen potential of the core electrons. The DF computational program is that used in Refs. 4 and 5.

We present our numerical results in both tabular and graphical form in Sec. II. We want to follow trends simultaneously in core and valence states as much as possible. Hence we focus initially on a subset of the neutral alkali-metal atoms. For these atoms, the frozen core consists of closed shells or subshells of a total of $Z-1$ electrons. We study the effective shielding as a function of principal quantum number for circular orbits, proceeding from the inner core to the valence states. We also study the dependence of shielding on the nuclear charge Z. Further, we analyze the relative importance of the Hartree and exchange effects, and of fine-structure corrections, as we vary Z, for convenient sets of n and l. Because of the limitations set by available calculations,[5] and of reasonable extensions of them which can be made, our study of correlation corrections for alkali-metal atoms is restricted to their valence states. In order to follow these trends to core states, we consider noble gases (a frozen core of a total of Z electrons in closed shells or subshells) of nuclear charges neighboring those of the alkali-metal atoms considered. Though no direct computations of these correlation contributions exist, estimates can be made, based on the availability of related computational results in the literature.[6,7] As is well known, and is also confirmed by our study of fine structure, relativistic effects contribute significantly only in core states. We therefore study one other such effect, the contribution due to the Breit interaction, by carrying out the computations of Ref. 4 for individual noble-gas core levels.

We summarize the trends in the correlation contribution, for selected valence levels of the alkali metals and core levels of the neighboring noble gases, as a function of the principal quantum number (restricting ourselves to s states). Lastly, we generate estimates for the various contributions to the energy on general semiquantitative grounds. Unfortunately, a simple-minded analysis, based on dimensional and general coupling and symmetry considerations alone, is not adequate for this purpose. This is due to the fact that overlap effects play a significant role, even in the estimation of orders of magnitude for the various contributions.

In Sec. III, we briefly summarize the qualitative features of our results.

II. NUMERICAL AND GRAPHICAL RESULTS

It is useful to provide an anchor to the presentation of calculational results by discussing the experimental information to which they correspond and which they approximate. If one were to deal with the exact many-electron atomic system, and suppress all but energy labels, one would describe the state of such an atom[8] in the Dirac notation by a ket $|{}^{M,(Z)}_{\sigma}\rangle$. In this ket, (Z) refers to the nuclear charge $-eZ$ (a label which was suppressed in Ref. 8), M to the lepton charge eM, and σ is an energy label. Note for purposes of orientation that, in the nonrelativistic limit and in the quasiparticle approximation of the Hartree-Fock theory, M is the number of electrons shielding the nucleus. (If e-e interactions are neglected, the label M is unnecessary, since the total energy is not affected by shielding.) The letter σ labels the total energy of the atom, $E_{\sigma}^{M,(Z)}$, with $\sigma=0$ corresponding to the ground state. Since this state must be nondegenerate in the analysis of Ref. 8, the label M in $E_{0}^{M,(Z)}$ must be a number corresponding to zero total spin for the M-electron system. The requirement of closed shells or subshells is a sufficient, but not necessary, condition for this. Again using the nonrelativistic Hartree-Fock theory as a guide, the energy labels $\sigma=a,p$ correspond to core and valence states, respectively. If we make no approximations, i.e., take H to be the exact Hamiltonian of the atom, we have

$$H\,|{}^{M,(Z)}_{\sigma}\rangle=E_{\sigma}^{M,(Z)}\,|{}^{M,(Z)}_{\sigma}\rangle\ . \tag{1}$$

One can use time translation operators and Eq. (1) to define[9] $e_{p}^{M,(Z)}$ and $e_{a}^{M,(Z)}$ from matrix elements of the lepton Heisenberg field operators,

$$\langle{}^{M,(Z)}_{0}|\,\psi(\mathbf{r},t)\,|{}^{M+1,(Z)}_{p}\rangle=e^{-ie_{p}^{M,(Z)}t}f_{p}^{M,(Z)}(\mathbf{r})\ , \tag{2}$$

$$\langle{}^{M,(Z)}_{0}|\,\psi^{\dagger}(\mathbf{r},t)\,|{}^{M-1,(Z)}_{a}\rangle=e^{+ie_{a}^{M,(Z)}t}[g_{a}^{M,(Z)}(\mathbf{r})]^{*}\ , \tag{3}$$

with

$$e_{p}^{M,(Z)}\equiv E_{p}^{M+1,(Z)}-E_{0}^{M,(Z)}\ , \tag{4}$$

$$e_{a}^{M,(Z)}\equiv E_{0}^{M,(Z)}-E_{a}^{M-1,(Z)}\ . \tag{5}$$

We emphasize that the total atom energies $E_{\sigma}^{M,(Z)}$ are the fundamental quantities, and that Eqs. (4) and (5) serve as definitions of $e_{p}^{M,(Z)}$ and $e_{a}^{M,(Z)}$, respectively. It is approximate values of these $e_{\sigma}^{M,(Z)}$ which are calculated in the DF approximation and corrections to it. These apparent single-electron energies are thus actually differences of many-electron atom energies. They are also quantities which have a direct experimental interpretation,[10] which we will now discuss.

Consider valence states for a neutral atom first, i.e., $E_{p}^{M+1,(Z)}\equiv E_{p}^{Z,(Z)}$, which fixes M to be

$$M=Z-1\ . \tag{6}$$

The definition of the corresponding $e_{p}^{Z-1,(Z)}$ involves $E_{0}^{Z-1,(Z)}$. The latter is the ground state of the singly ionized atom with nuclear charge Z. (The frozen core in the DF approximation consists of the inner $Z-1$ electrons, which, for example, form closed shells or subshells. This criterion includes the cases of the alkali atoms.) Thus $e_{p}^{Z-1,(Z)}$ is the ionization energy of the valence state labeled by p.

We turn next to the identification of the electron-hole states, labeled a, which correspond to the valence-electron states just discussed. These are the states which appear in the potential of the DF approximation. Thus we still consider the alkali-metal atoms and focus first on the $E_{p}^{Z,(Z)}$, the energies of our primary concern. These energies serve to fix the relevant ground state to be $E_{0}^{Z-1,(Z)}$. Since the same ground state plays a role in the definition of the electron-hole states needed in the DF approximation [see Eqs. (4) and (5)], these states must have $Z-2$ shielding electrons. In other words, they are states of a doubly ionized atom, with energies $E_{a}^{Z-2,(Z)}$. If one uses the quasiparticle description, one can say that these energies are those of an atom with the outermost-core electron and an inner-core electron absent. The energy $e_{a}^{Z-1,(Z)}$ thus represents a satellite, rather than a first-order, x-ray line. It corresponds to a transition where an electron of zero kinetic energy, infinitely far from a doubly ionized atom, drops into the hole in the inner shell. Finally, one has a singly ionized atom in its ground state.

Accurate experimental data exist for valence-state ionization energies,[11,12] and are listed in column 3 of Table I. This is not the case for the core states $E_{a}^{Z-2,(Z)}$, and the corresponding $e_{a}^{Z-1,(Z)}$, the satellite x-ray lines. Only limited, and somewhat outdated, information[13] exists for these, and even their proper identification is often somewhat uncertain.

Our primary focus in the present work is, in any case, on the study of the general way in which energies depend on various parameters in the DF approximation, and corrections to it, and not on a detailed comparison with experiment. Since, as much as possible, we would like to study various trends as we pass from core to valence states, we list the calculated results for various quantities of interest in columns 4, 5, and 6 of Table I for both these types of states, even though no direct comparison of the DF energies of column 3 to experimental values is available for core states.

In order to obtain an indication of the size of relativistic effects as they are reflected in fine structure, we give the ratio of fine-structure energy differences, as calculated in the DF approximation, to the average DF energy for the states (n,l), in column 5 of Table I. The criterion for the inclusion of an entry in this column is that the ratio of DF fine structure to the DF energy exceeds 0.001. For the four cases [all the lowest lying valence (np) states] for which comparison is possible between experiment and DF fine structure, the two agree both in sign and order of magnitude to a few tenths of a percent. Thus, it is not unreasonable to use DF results as estimates for these relativistic effects in core states, where their contribution is more significant than for valence states.

In column 6 of Table I, we give the relative size of the exchange X and Hartree, or "tadpole"[8] T contributions to the DF energies. The entries in this column arise from solving the DF problem first, and then using the DF wave functions which one obtains to calculate the energy contributions

TABLE I. Alkali-metal atoms—experimental and calculated data ($p^* = p_{1/2}, p = p_{3/2}$, etc).

Atom	State	Expt[a]	Calculation				
			Dirac-Fock				
	(σ)	e_σ^{expt}	$\varepsilon_\sigma^{\text{DF}}$	$\frac{\Delta\varepsilon_{\text{L}\cdot\text{S}}^{\text{DF}}}{\varepsilon^{\text{DF}}}$	$-X/T$	$\frac{\Delta\varepsilon^{\text{corr}}}{\varepsilon^{\text{DF}}}$	$\frac{\varepsilon^{\text{expt}}-\varepsilon^{\text{DF}}}{\varepsilon^{\text{DF}}}$
^{11}Na	1s		−40.826 55		0.260		
(3s)^1	2s		−3.082 40		0.158		
	2p^*		−1.801 42	0.004	0.132		
	2p	−1.738 14	−1.794 01		0.132		−0.031
	3s	−0.188 90	−0.182 03		0.007	0.032	0.038
	3p^*	−0.111 62	−0.109 49	0.001	0.003	0.016	0.019
	3p	−0.111 55	−0.109 42		0.003	0.016	0.019
	4s	−0.071 60	−0.070 16		0.004	0.018	0.020
	3d	−0.055 95	−0.055 67		0.000	0.004	0.005
	4p	−0.050 94	−0.050 31		0.002		0.012
	5s	−0.037 59	−0.037 06		0.003		0.014
	4d	−0.031 45	−0.031 32		0.000		0.004
	4f	−0.031 27	−0.031 25		0.000		
^{19}K	1s		−134.399 46		0.211		
(4s)^1	2s		−14.823 35		0.127		
	2p^*		−11.818 29	0.009	0.111		
	2p		−11.708 80		0.111		
	3s		−1.977 10		0.087		
	3p^*		−1.177 44	0.009	0.073		
	3p	−1.162 46	−1.166 44		0.073		−0.003
	4s	−0.159 55	−0.147 49		0.005	0.084	0.082
	4p^*	−0.100 37	−0.095 71	0.002	0.003	0.048	0.049
	4p	−0.100 11	−0.095 50		0.003	0.048	0.048
	5s	−0.063 72	−0.061 09		0.003	0.048	0.043
	3d^*	−0.061 40	−0.058 07		0.002	0.048	0.057
	3d	−0.061 41	−0.058 08		0.002	0.047	0.057
	5p	−0.046 89	−0.045 55		0.002		0.029
	6s	−0.034 45	−0.033 44		0.002		0.030
	4d	−0.034 69	−0.032 84		0.002		0.056
	4f	−0.031 36	−0.031 25		0.000		0.004
^{37}Rb	1s		−562.337 29		0.161		
(5s)^1	2s		−77.705 32		0.092		
	2p^*		−70.220 59	0.033	0.084		
	2p		−67.968 32		0.084		
	3s		−12.763 25		0.069		
	3p^*		−10.022 14	0.036	0.069		
	3p		−9.668 74		0.063		
	3d^*		−4.879 68	0.012	0.053		
	3d		−4.819 66		0.053		
	4s		−1.767 12		0.044		
	4p^*		−1.033 77	0.036	0.038		
	4p		−0.997 64		0.037		
	5s	−0.153 51	−0.139 29		0.003	0.108	0.102
	5p^*	−0.096 19	−0.090 82	0.009	0.001	0.060	0.059
	5p	−0.095 11	−0.089 99		0.002	0.058	0.057
	4d	−0.065 32	−0.059 74		0.002	0.080	0.093
	6s	−0.061 77	−0.058 70		0.002	0.059	0.052
	6p	−0.045 08	−0.043 60		0.001		0.034
	5d	−0.036 37	−0.033 77		0.002		0.077
	4f	−0.031 41	−0.031 26		0.000		0.005
^{55}Cs	1s		−1330.122 63		0.140		
(6s)^1	2s		−212.564 91		0.080		
	2p^*		−199.429 42	0.067	0.074		
	2p		−186.436 53		0.073		
	3s		−45.969 83		0.059		

TABLE I. (*Continued*).

Atom	State	Expt[a]	Calculation				
			Dirac-Fock				
	(σ)	e_σ^{expt}	$\varepsilon_\sigma^{\text{DF}}$	$\frac{\Delta\varepsilon_{\text{L}\cdot\text{S}}^{\text{DF}}}{\varepsilon^{\text{DF}}}$	$-X/T$	$\frac{\Delta\varepsilon^{\text{corr}}}{\varepsilon^{\text{DF}}}$	$\frac{e^{\text{expt}}-\varepsilon^{\text{DF}}}{\varepsilon^{\text{DF}}}$
	$3p^*$		−40.448 29	0.065	0.055		
	$3p$		−37.894 29		0.054		
	$3d^*$		−28.909 49	0.040	0.048		
	$3d$		−27.775 15		0.048		
	$4s$		−9.512 84		0.045		
	$4p^*$		−7.446 28	0.073	0.042		
	$4p$		−6.921 00		0.042		
	$4d^*$		−3.485 62	0.026	0.034		
	$4d$		−3.396 90		0.034		
	$5s$		−1.489 81		0.030		
	$5p^*$		−0.907 90	0.077	0.026		
	$5p$		−0.840 34		0.026		
	$6s$	−0.143 10	−0.127 37		0.002	0.139	0.123
	$6p^*$	−0.092 17	−0.085 62	0.022	0.001	0.081	0.076
	$6p$	−0.089 64	−0.083 79		0.001	0.074	0.070
	$5d$	−0.076 59	−0.064 53		0.003	0.168	0.187
	$7s$	−0.058 65	−0.055 19		0.001	0.076	0.063
	$4f$	−0.031 57	−0.031 27		0.000		0.010

[a]Data for Na and K are taken from Ref. 12; those for Rb and Cs, from Ref. 11.

$$T \equiv \varepsilon_\sigma^{Z-1,(Z)}(T) = \alpha \sum_{a=1}^{Z-1} V_{a\sigma;a\sigma}^{\text{Coul}} , \tag{7}$$

$$X \equiv \varepsilon_\sigma^{Z-1,(Z)}(X) = -\alpha \sum_{a=1}^{Z-1} V_{a\sigma;\sigma a}^{\text{Coul}} , \tag{8}$$

with

$$V_{\kappa\lambda;\mu\nu}^{\cdots} \equiv \int d1\,d2\,\phi_\kappa^\dagger(1)\phi_\mu(1)\phi_\lambda^\dagger(2)\phi_\nu(2)V^{\cdots}(r_{12}) , \tag{9}$$

and

$$V^{\text{Coul}}(r_{12}) = 1/r_{12} = 1/|\mathbf{r}_1-\mathbf{r}_2| = 1/|1-2| , \tag{10}$$

where the symbols ε and ϕ refer to energies and wave functions in the DF approximation. The ratio $-X/T$, given in column 6 of Table I is the number obtained from the results calculated for Eqs. (7) and (8).

The seventh column in Table I gives the ratio of the correlation energy, as calculated by the method of Ref. 5, to the corresponding DF energy. The expressions which must be evaluated to obtain the correlation contribution are[8]

$$\Delta\varepsilon_\sigma^{\text{corr}} = \alpha^2 \left[\sum_{a,c=1}^{M} \sum_{p=M+1}^{\infty} \frac{(V_{ca;\sigma p}^{\text{Coul}} - V_{ac;\sigma p}^{\text{Coul}})V_{p\sigma;ca}^{\text{Coul}}}{e_{ac}^{\sigma p}} - \sum_{b=1}^{M} \sum_{p,q=M+1}^{\infty} \frac{V_{b\sigma;qp}^{\text{Coul}}(V_{qp;\sigma b}^{\text{Coul}} - V_{qp;b\sigma}^{\text{Coul}})}{e_{\sigma b}^{qp}} \right] , \tag{11}$$

with

$$e_{\kappa\lambda}^{\mu\nu} = (\varepsilon_\kappa + \varepsilon_\lambda - \varepsilon_\mu - \varepsilon_\nu)^{\text{DF}} . \tag{12}$$

The ε^{DF} on the right-hand side of Eq. (12) are the appropriate DF energies. For alkali-metal atoms, $M = Z-1$, from Eq. (6). Equation (11) is the correlation energy contribution with nonvanishing nonrelativistic limit. The pair terms in the correlation energy[14] can be neglected in the present approximation.

Only the numbers listed in column 7 of Table I are available from the work of Johnson *et al.*[5] A good estimate for the approximate correlation energy contribution $\Delta\varepsilon_{\text{appr}}^{\text{corr}}$ for valence states is given by

$$\Delta\varepsilon_{\text{appr}}^{\text{corr}} \approx e^{\text{expt}} - \varepsilon^{\text{DF}} , \tag{13}$$

as can be seen from a comparison of columns 7 and 8 of Table I. We will therefore extend the estimates of correlation energy contributions to those valence states for which no direct calculations are available, in order to facilitate our study of trends in the behavior of this quantity. We exclude those values of the estimate as unreliable, which are so small as to be comparable to the differences between columns 7 and 8 of Table I.

We would also like to tie to experiment our study of the Breit interaction contributions to energy levels for the core states. In addition, since no direct calculations of correlation corrections are presently available,[15] we would like to obtain approximations of these corrections from results in the current literature. In order to accomplish these aims, we focus on the core states, with energy $E_a^{M-1,(Z)}$, and demand that they correspond to first-order x-ray edges. Thus we fix

$$M=Z\ , \tag{14}$$

and the relevant ground state becomes $E_0^{Z,(Z)}$. This set of conditions describes the noble gases, for example. We will not be concerned with valence states sharing the same ground state $E_0^{Z,(Z)}$. These would be states of negative ions, and are not of interest to us here. The largest relativistic contributions are, in any case, expected to come from the deep core states, and we do not need additional estimates of correlation contributions for valence states.

We list experimental and calculated data for the core states of the noble gases (with nuclear charge one unit less than those of the alkali-metal atoms previously considered) in Table II. Columns 1–4 of this table correspond to the same column numbers[16] in Table I. We will not repeat our consideration of fine-structure effects for these atoms, since they do not provide new information of interest. In the fifth column, we list the ratio of Breit interaction contributions to the DF energies. In the sixth column of Table II, we give the ratio of the estimated approximate correlation energy contribution (as far as it is available from the current literature) to the DF energies. These approximate correlation energies, for deep-lying core states only, are given by the relaxation correction to the frozen orbital energy[6,7] (R_a of Ref. 6). This assertion will be justified in more detail below. We cannot estimate $\Delta\varepsilon^{\text{corr}}$ for these deep core states in the same way as we did for the valence states, since relativistic (both Breit and radiative) corrections are expected to contribute significantly[4] to the experimental energies for these states.

The Breit interaction contributions for the noble gases are

$$\Delta\varepsilon_\sigma^{\text{Breit}}=[\Delta\varepsilon(T)+\Delta\varepsilon(X)]_\sigma^{\text{Breit}}\ , \tag{15}$$

where

$$\begin{aligned}\Delta\varepsilon(T)_\sigma^{\text{Breit}}&=\alpha\sum_{a=1}^{Z}V_{a\sigma;a\sigma}^{\text{Breit}}\ ,\\ \Delta\varepsilon(X)_\sigma^{\text{Breit}}&=-\alpha\sum_{a=1}^{Z}V_{a\sigma;\sigma a}^{\text{Breit}}\ ,\end{aligned} \tag{16}$$

and

$$V^{\text{Breit}}(\mathbf{r}_{12})=-(\boldsymbol{\alpha}_1\cdot\boldsymbol{\alpha}_2+\boldsymbol{\alpha}_1\cdot\hat{\mathbf{n}}_{12}\,\boldsymbol{\alpha}_2\cdot\hat{\mathbf{n}}_{12})/2r_{12}\ . \tag{17}$$

TABLE II. Noble gases—experimental and calculated data ($p=p_{3/2}$, $d=d_{5/2}$).

Atom	State	Expt[a]	Calculation		
	(σ)	e_σ^{expt}	$\varepsilon_\sigma^{\text{DF}}$	$\dfrac{\Delta\varepsilon^{\text{Breit}}}{\varepsilon^{\text{DF}}}$	$\dfrac{\Delta\varepsilon_{\text{appr}}^{\text{corr}}}{\varepsilon_{\text{DF}}}$
^{10}Ne	1*s*	−31.9822	−32.81745	0.00042	−0.025
$(2p)^6$	2*s*	−1.7816	−1.93584	0.00041	−0.080
	2*p*	−0.7925	−0.84827	0.00074	−0.066
^{18}Ar	1*s*	−117.8521	−119.12658	0.00079	−0.011
$(3p)^6$	2*s*	−11.9828	−12.41158	0.00063	−0.034
	2*p*	−9.1326	−9.54706	0.00086	−0.043
	3*s*	−1.0748	−1.28659	0.00061	−0.165
	3*p*	−0.5793	−0.58782	0.00097	−0.014
^{30}Kr	1*s*	−526.5659	−529.68523	0.00163	−0.006
$(4p)^6$	2*s*	−70.6102	−72.07982	0.00128	−0.020
	2*p*	−61.5643	−62.87919	0.00166	−0.021
	3*s*	−10.7367	−11.22446	0.00136	−0.043
	3*p*	−7.8807	−8.31279	0.00185	−0.052
	3*d*	−3.4485	−3.72679	0.00194	−0.075
	4*s*		−1.18775	0.00135	
	4*p*		−0.51435	0.00214	
^{54}Xe	1*s*	−1270.3560	−1277.26097	0.00248	−0.005
$(5p)^6$	2*s*	−200.4015	−202.46547	0.00189	−0.010
	2*p*	−175.7793	−177.70452	0.00236	−0.011
	3*s*	−42.1938	−43.01054	0.00180	−0.019
	3*p*	−34.4321	−35.32526	0.00226	−0.025
	3*d*	−24.7999	−25.53709	0.00192	−0.029
	4*s*		−8.42994	0.00195	
	4*p*		−5.98279	0.00254	
	4*d*		−2.63376	0.00261	
	5*s*		−1.01014	0.00212	
	5*p*		−0.43980	0.00319	

[a] Reference 16.

The vector $\hat{\mathbf{n}}_{12}$ is a unit vector in the direction of $\mathbf{r}_{12}$.

Only the exchange contributions of the Breit interaction are nonvanishing. This fact is pointed out in Ref. 4, among other places. Without using the detailed arguments of Ref. 4, one can show it by going to momentum space. The Breit interaction in momentum space has the form

$$V^{\mathrm{Breit}}(\mathbf{k})=\alpha_{1_i}\alpha_{2_j}[\delta_{ij}-(k_ik_j)/\mathbf{k}^2](1/\mathbf{k}^2) . \tag{18}$$

Evaluation of $\Delta\varepsilon^{\mathrm{Breit}}(T)$ involves taking expectation values of (18) and carrying out a spherical average. Matrix elements of α_{1_i} (or α_{2_j}) will thus separately be proportional to k_i. The effect of one of these is sufficient to make $\Delta\varepsilon^{\mathrm{Breit}}(T)$ vanish.[17]

In order to determine, without specific calculations, the relative importance of the various energy contributions which appear in Tables I and II, we want to make crude estimates for these contributions, based on general arguments. The aim of these estimates is to provide a qualitative understanding of the significant physical and mathematical elements which enter into the calculation of these terms, to understand the trends to be expected as functions of levels and nuclear charges, and thus to serve as a guide for future calculations. We will test the validity of these crude estimates by comparing them to the experimental and calculated results listed in Tables I and II.

We write for a given level

$$e_\sigma=\varepsilon_\sigma^{\mathrm{DF}}+\Delta\varepsilon_\sigma^{\mathrm{Breit}}+\Delta\varepsilon_\sigma^{\mathrm{ret}}+\Delta\varepsilon_\sigma^{\mathrm{corr}}+\cdots , \tag{19}$$

where $\varepsilon_\sigma^{\mathrm{DF}}$ is the DF approximation to the exact many-electron atomic energy difference e_σ, and the various $\Delta\varepsilon$'s have been defined above.

Our order-of-magnitude estimates are based on assuming that the DF approximation is roughly equivalent to a central field approximation, that the field goes approximately as $1/r$, and that the electron in the state σ sees an effective charge $Z_{\mathrm{eff}}(\sigma)$. The assumption of an effective $1/r$ dependence leads to the virial theorem result[18]

$$\varepsilon_\sigma^{\mathrm{DF}}\approx\tfrac{1}{2}[\varepsilon^{\mathrm{Nuc}}+\varepsilon(T)+\varepsilon(X)]_\sigma , \tag{20}$$

where

$$\varepsilon_\sigma^{\mathrm{Nuc}}=-\alpha Z\int d\mathbf{r}\frac{1}{r}\,|\phi_\sigma(\mathbf{r})|^2 . \tag{21}$$

To estimate $\varepsilon^{\mathrm{Nuc}}$, we take

$$\int d\mathbf{r}(1/r)\,|\phi_{n,l}(\mathbf{r})|^2\approx\alpha Z_{\mathrm{eff}}(n,l)/n^2,\quad \sigma\equiv(n,l) . \tag{22}$$

To characterize roughly Coulomb energies between two electrons in Eq. (20), we let $\mathbf{r}_1\rightarrow 0$ in the $|\mathbf{r}_1-\mathbf{r}_2|$ term, if $\mathbf{r}_1$ is the coordinate of a core state. Because of the orthogonality of the single-particle states, this will imply that all terms occurring in the sums over a in the exchange energy, Eq. (8), will vanish, except for the term for which $a=\sigma$. (For σ a valence state, no such term exists.) Further, in the T term, Eq. (7), we will assume, in analogy with the classical electrostatic result, that only those core electrons, the "orbits" of which lie "inside" the electron "orbit" associated with the σ level, will contribute to the sum. Call the number of such electrons $N_{\mathrm{eff}}(\sigma)$. We may expect that

$$N_{\mathrm{eff}}(\sigma)\approx Z-Z_{\mathrm{eff}} . \tag{23}$$

These rough approximations lead to

$$(\varepsilon_{n,l}^{\mathrm{DF}})^{\mathrm{est}}\approx\alpha^2/2n^2[-\alpha Z_{\mathrm{eff}}(n,l)Z+\alpha N_{\mathrm{eff}}(n,l)Z_{\mathrm{eff}}(n,l)-\alpha Z_{\mathrm{eff}}(n,l)] \tag{24}$$

for (n,l) a core state. The last term in Eq. (24) is absent in valence states. It will also be dropped for core states, in the spirit of our approximation. We thus have an estimate for DF energies, for both core and valence states, using (20) and (23),

$$(\varepsilon_{n,l}^{\mathrm{DF}})^{\mathrm{est}}\approx-\alpha^2Z_{\mathrm{eff}}^2(n,l)/2n^2 . \tag{25}$$

The value of $Z_{\mathrm{eff}}(n,l)$ is fitted by setting $(\varepsilon_{n,l}^{\mathrm{DF}})^{\mathrm{est}}\equiv\varepsilon_{n,l}^{\mathrm{DF}}$, where the $\varepsilon_{n,l}^{\mathrm{DF}}$ are entries in column 4 of Tables I and II. $Z_{\mathrm{eff}}(n,l)$ is listed in column 3 of Tables III and IV.

We next study the trends in the $Z_{\mathrm{eff}}(n,l)$ we have obtained. In Fig. 1, we provide a semilogarithmic plot of $Z_{\mathrm{eff}}(n,l_{\max})$, $l_{\max}=n-1$, (circular electron orbits) as a function of n, for the four alkali-metal atoms we have considered. (The lines connecting the discrete data points in this and subsequent figures are provided only to guide the eye.) We stop the analysis when Z_{eff} reaches, or goes below, 1.01. We note that this is achieved for a principal quantum number which is that of the ground-state outermost s electron for Na and K, and for $4f$ electrons, which thus have principal quantum numbers below that of the ground state, for Rb and Cs. All these levels have energies which are higher than that of the ground-state (ns) valence electron. For $Z_{\mathrm{eff}}\cong 1.01$, we can say that the core completely shields the nucleus.

In Fig. 2, orbital angular momentum dependence of $Z_{\mathrm{eff}}(n_0,l)$ is illustrated. The fixed value n_0 is chosen so that, for each alkali-metal atom, full shielding is achieved

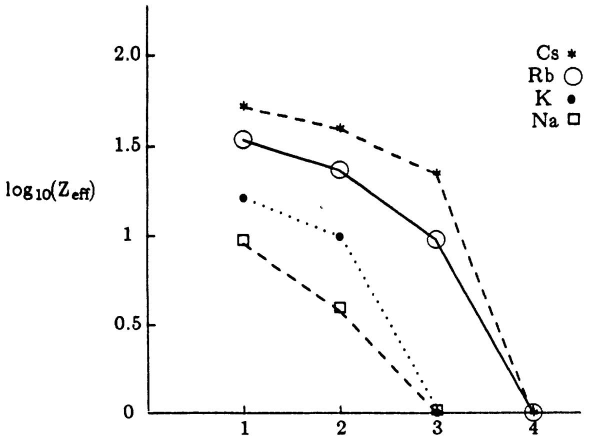

FIG. 1. $Z_{\mathrm{eff}}(n,l_{\max})$, $l_{\max}=n-1$, for four alkali-metal atoms.

TABLE III. Alkali-metal atoms—tests of energy contribution estimates ($p = p_{3/2}$, $d = d_{5/2}$, $f = f_{7/2}$).

Atom	State (σ)	Z_{eff}	F_x Eq. (28)	F_{corr} Eq. (31)	$F_{\text{L}\cdot\text{S}}$ Eq. (33)
^{11}Na	1s	9.0	1.923		
$(3s)^1$	2s	5.0	1.055		
	2p	3.8	1.052		0.8
	3s	1.8		1.71	
	3p	1.4		3.84	2.1
	4s	1.5		1.77	
	3d	1.0			
	4p	1.3		3.36	
	5s	1.4		1.88	
	4d	1.0			
	4f	1.0			
^{19}K	1s	16	1.580		
$(4s)^1$	2s	11	0.984		
	2p	9.7	0.969		1.1
	3s	6.0	0.884		
	3p	4.6	0.951		0.7
	4s	2.2		0.76	
	4p	1.7		1.28	2.4
	5s	1.7		0.92	
	3d	1.0		2.20	
	5p	1.5		1.35	
	6s	1.6		0.91	
	4d	1.0		1.26	
	4f	1.0			
^{37}Rb	1s	34	2.070		
$(5s)^1$	2s	25	0.906		
	2p	23	0.850		1.1
	3s	15	0.659		
	3p	13	0.661		0.7
	3d	9.4	0.684		1.0
	4s	7.5	0.770		
	4p	5.6	0.861		0.5
	5s	2.6		0.52	
	5p	2.1		1.06	1.6
	4d	1.4		1.12	
	6s	2.0		0.80	
	6p	1.8		1.23	
	5d	1.3		0.87	
	4f	1.0			
^{55}Cs	1s	52	2.381		
$(6s)^1$	2s	41	0.893		
	2p	39	0.856		1.2
	3s	30	0.678		
	3p	27	0.661		0.8
	3d	22	0.631		0.7
	4s	17	0.585		
	4p	15	0.595		0.6
	4d	10	0.654		0.8
	5s	8.6	0.718		
	5p	6.5	0.793		0.4
	6s	3.0		0.24	
	6p	2.4		0.46	1.2
	5d	1.8		0.25	
	7s	2.3		0.38	
	4f	1.0			

TABLE IV. Noble gases—tests of energy contribution estimates ($p = p_{3/2}$, $d = d_{5/2}$).

Atom	State (σ)	Z_{eff}	F_{corr} Eq. (31)	F_{Breit} Eq. (35)
^{10}Ne	1*s*	8.1	−0.40	1.57
$(2p)^6$	2*s*	3.9	−1.80	1.67
	2*p*	2.6		1.38
^{18}Ar	1*s*	15	−1.52	1.46
$(3p)^6$	2*s*	10	−0.72	1.37
	2*p*	8.7	−0.67	1.15
	3*s*	4.8	−0.45	1.96
	3*p*	3.2		1.85
^{30}Kr	1*s*	32	−0.89	1.32
$(4p)^6$	2*s*	24	−0.62	1.12
	2*p*	22	−1.07	0.94
	3*s*	14	−0.88	1.21
	3*p*	12	−0.93	1.04
	3*d*	8.2	−0.91	1.45
	4*s*	6.2		2.06
	4*p*	4.0		2.02
^{54}Xe	1*s*	50	−0.35	1.25
$(5p)^6$	2*s*	40	−0.59	1.03
	2*p*	38	−0.77	0.87
	3*s*	28	−0.55	1.03
	3*p*	25	−0.56	0.92
	3*d*	21	−0.87	1.28
	4*s*	16		1.24
	4*p*	14		1.09
	4*d*	9.2		1.62
	5*s*	7.1		2.06
	5*p*	4.7		2.07

for $Z_{\text{eff}}(n_0, l_{\max})$. As expected, the l-dependence of Z_{eff}, for fixed n_0, is much less rapid than its n dependence for circular orbits. Also, since orbits of lower l sample regions closer to the nucleus than those of higher l (for fixed n_0), electron shielding is less effective for the former than for the latter.

The trends in the X contributions are harder to characterize. Overlap, which is a consequence of detailed evaluation of the integrals in Eq. (8), and not of any general dimensional or coupling-constant considerations, plays the crucial role. We estimate these integrals as indicated in the discussion below Eq. (22), resulting in

$$-(X/T)_{\sigma}^{\text{est}} \approx 1/N_{\text{eff}}(\sigma) \tag{26}$$

for core states, and

$$-(X/T)_{\sigma}^{\text{est}} \approx 0 \tag{27}$$

for valence states.

To test the validity of these estimates, we compare them to calculated values of $-(X/T)$, given in column 6 of Table I. We note the sharp drop in the values of $-(X/T)$, as the valence states are reached, justifying the estimate of Eq. (27). For core states, we test our estimate in Eq. (26) by defining the ratio of the estimated and calculated values of $-(X/T)$ to be

$$F_X \equiv -1/[(X/T)N_{\text{eff}}] \ . \tag{28}$$

If our rough estimates make sense, we can expect F_X to be of $O(1)$. We give the values of F_X in column 4 of Table III. They are not unreasonable.

As expected, the overlap, and hence the magnitude of X/T, decreases rapidly as one proceeds from inner to outer shells. We illustrate this effect in Fig. 3, using the calculated data of Table I directly. Figure 3 is a plot of $-(X/T)(n, l_{\max})$ versus n, for our subset of alkali-metal atoms.

Correlation terms (which fall in the general category of exchange effects) are even harder to characterize than the X terms in the DF approximation. Due to their exchange aspect, correlation terms should depend on overlap in some way; further, from the point of view of classical electrostatics, they should be proportional to the enclosed shielding electron charge for the orbit (n,l); lastly, they contain energy denominators.

To estimate $\Delta\varepsilon^{\text{corr}}$, we first eliminate all but the maximum overlap terms. That is, we keep only those terms

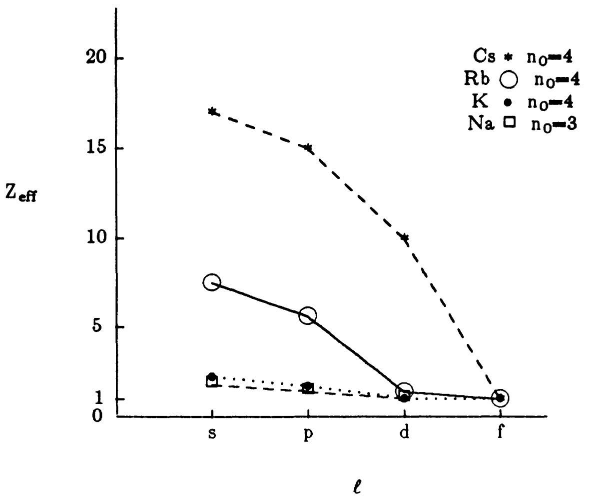

FIG. 2. $Z_{\text{eff}}(n_0, l), n_0$ fixed, for four alkali-metal atoms.

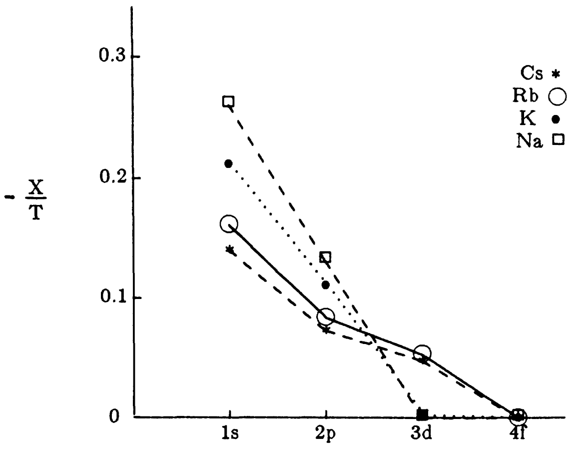

FIG. 3. Relative magnitude of exchange X and Hartree T contributions as function of $n, l_{\max}$ for four alkali-metal atoms.

in Eq. (11) in which all the expectation values of V^{Coul} are of form $V^{\text{Coul}}_{\sigma\mu;\sigma\nu}$ or $V^{\text{Coul}}_{\mu\sigma;\nu\sigma}$. This means that the dominant terms in the sums of Eq. (11) are the second for core states, with only the single term $a=\sigma$ surviving from the sum over a, and the fourth for valence states, with only the single term $p=\sigma$ surviving from the sum over p. The dominant terms which thus remain are

$$\Delta\varepsilon^{\text{corr}}_{\text{core}} \cong -\alpha^2 \sum_{c,p} | V^{\text{Coul}}_{\sigma c;\sigma p} |^2 / e^p_c \tag{29}$$

for core states, and

$$\Delta\varepsilon^{\text{corr}}_{\text{val}} \cong \alpha^2 \sum_{b,q} | V^{\text{Coul}}_{q\sigma;b\sigma} |^2 / e^q_b \tag{30}$$

for valence states, where the conventions of Eq. (12) are used in the energy denominators.

We observe that Eq. (29) is closely related to the expression obtained for the rearrangement energy which results from the solution of DF equations based on variational principles, involving Lagrange multipliers for open shells.[6,7] In order to make a detailed comparison, it is of course necessary to treat rearrangement and correlation in a parallel fashion, i.e., in perturbation theory.[7,19] This argument justifies our use in Table II of values obtained for rearrangement energies[6] as estimates for correlation energies for the noble gases. Note further that the contributions of (29) and (30) are positive and negative, respectively (since the energy denominators are negative in both cases). The ratios of correlation contributions to DF energies are thus positive for valence and negative[6] for core states. This is numerically confirmed by the calculational results listed in columns 7 and 8 of Table I, and column 7 of Table II, respectively.

Next, let us use the calculational results and the estimates for correlation effects in Tables I and II to study the interplay of exchange and charge enclosure effects, without any reference to crude approximations. We illustrate these trends in Figs. 4 and 5, in which we plot the relative size of correlation contributions in s states, as a function of n, for the alkali metals and related noble gases. (There are points missing in the figure, for values of n for which even estimated values are unavailable.) We note an initial rise in the magnitude of the correlation with increasing n, l, or j, as more and more charge is enclosed by an orbit. Eventually, the reduction of overlap (due to the exchange aspect of the correlation) serves to control its value, and we see the anticipated drop. Correlation effects also increase in magnitude with Z, as one would expect.

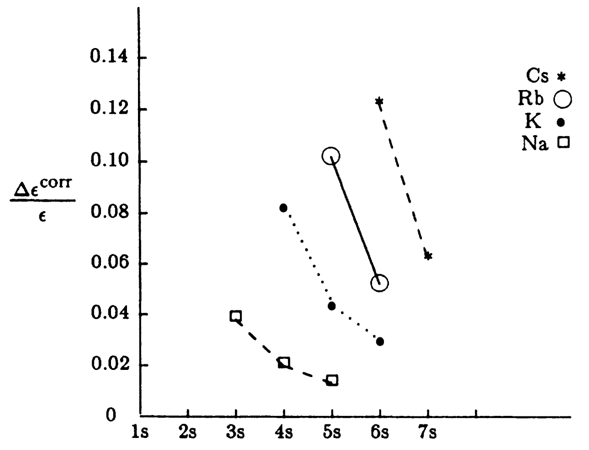

FIG. 4. $\Delta\varepsilon^{\text{corr}}/\varepsilon$ for four alkali-metal atom valence s states.

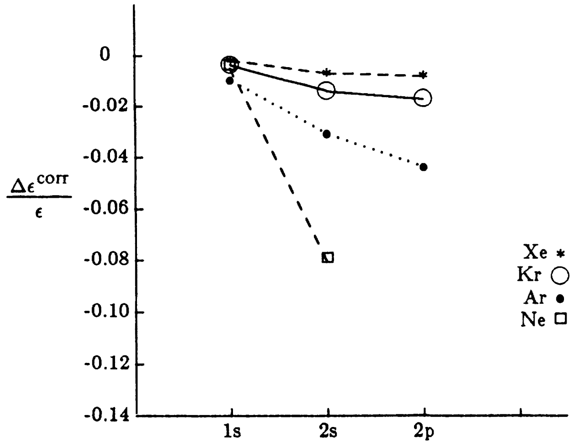

FIG. 5. $\Delta\varepsilon^{\text{corr}}/\varepsilon$ of low-lying states for noble-gas atoms.

To obtain an order-of-magnitude estimate of the correlation effects, Eqs. (29) and (30), we keep only those terms in the sums which do not vanish because of wave-function orthogonality, when we set either $\mathbf{r}_1$ or $\mathbf{r}_2$ in $|\mathbf{r}_1-\mathbf{r}_2|$ equal to zero (depending on whether $\mathbf{r}_1$ or $\mathbf{r}_2$ is the argument of the orbital of smaller average radius). We approximate the energy denominators which appear by ε_c alone. The sum over p (or q) can now be carried out. However, since these valence states are not complete, we put in a factor $0<f<1$, of $O(1)$, rather than unity, to account for this fact. (We have set $f=\frac{1}{3}$ in Tables III and IV.) We finally use the estimate (22), to obtain

$$(\Delta\varepsilon^{\text{corr}}_{\sigma})^{\text{est}} \approx \begin{cases} -f\alpha^2 \left[\dfrac{\alpha Z_{\text{eff}}}{2n^2(\sigma)}\right]^2 \displaystyle\sum_{c=1}^{N_{\text{eff}}(\sigma)} \frac{1}{e_c} \quad (\text{core}) & (31\text{a}) \\ +f\alpha^2 \left[\dfrac{\alpha Z_{\text{eff}}}{2n^2(\sigma)}\right]^2 \displaystyle\sum_{c=1}^{N_{\text{eff}}(\sigma)} \frac{1}{e_c} \quad (\text{val})\ . & (31\text{b}) \end{cases}$$

We test the estimate (31), by defining the ratio of (31) to the $\Delta\varepsilon^{\text{corr}}$ in Tables I and II to be F_{corr}. (Notice that the approximate $\Delta\varepsilon^{\text{corr}}$ for alkali-metal valence states are the entries in column 8 of Table I, multiplied by ε_σ, and for noble-gas core states are the entries in column 7 of Table II, multiplied by ε_σ.) We give the values of F_{corr} for valence states in column 5 of Table III, and for core states in column 4 of Table IV. The estimate, Eq. (31), is unreliable for the higher-lying core states, since it is overly sensitive to $N_{\text{eff}}(\sigma)$ for these states (and thus, indirectly, also to the approximation $e^p_c \approx e_c$). We therefore do not give values of F_{corr} for these states.

We can provide less detailed justification for our semiquantitative estimates of the various relativistic effects we wish to consider than we did for the cases where nonrelativistic limits existed for the various contributions. Let us consider fine-structure (FS) effects first. In the Coulomb-Dirac case, for a nucleus of charge αZ, the FS arises from a potential

$$(\alpha Z/m^2)(\sigma\cdot\mathbf{L}/r^3) .$$

It remains to be determined what the effective screening of the nucleus should be for the many-electron atoms of concern in this paper. We note that $1/r^3$ probes the vicinity of the nucleus more than $1/r$, since it is more singular at the origin. The relevant charge for this case should therefore lie between Z and Z_{eff}. We thus take our estimate for this case to be

$$(\Delta\varepsilon_{\mathbf{L}\cdot\mathbf{S}})_{n,l}^{\text{est}} \approx \alpha^4[Z_{\text{eff}}(n,l)Z]^2/2n^3 l . \tag{32}$$

We define the ratio of the estimated to the calculated values for the FS to be

$$F_{\mathbf{L}\cdot\mathbf{S}} = \frac{[(\alpha Z)^2/nl]}{(\Delta\varepsilon_{\mathbf{L}\cdot\mathbf{S}}^{\text{DF}})_{n,l}/\varepsilon_{n,l}^{\text{DF}}} . \tag{33}$$

Values of $F_{\mathbf{L}\cdot\mathbf{S}}$ are given in column 6 of Table III, for all the data available from Table I. This estimate proves to be adequate as well.

In the case of the Breit interaction, the presence of the Dirac α_i, $i=1,2$, would again tend to reduce the effect of shielding. In addition, since only exchange terms contribute, we will still assume that it is essentially one term which will dominate the sum. We conjecture

$$(\Delta\varepsilon_{n,l}^{\text{Breit}})^{\text{est}} \approx \alpha^4[Z_{\text{eff}}(n,l)Z^2]/2n^3 , \tag{34}$$

and a corresponding testing ratio

$$F_{\text{Breit}} = \frac{(\alpha Z)^2/nZ_{\text{eff}}}{\Delta\varepsilon^{\text{Breit}}/\varepsilon^{\text{DF}}} . \tag{35}$$

Values for this ratio are listed in column 5 of Table IV.

III. DISCUSSION

The relative magnitudes of the various contributions to many-electron atom energies can be semiquantitatively accounted for in a coherent and physically reasonable way, as can be seen from the details given in Sec. II above. That section served to confirm the approach taken in Ref. 14 to the estimation of these orders of magnitude, at least as far as they can be tested in the present paper. We summarize briefly: Shielding by inner electrons improves as one goes to circular electron orbits of larger and larger radius, reaching a maximum when all core electrons shield the nucleus. Again, shielding improves as one goes from orbits of greater penetration into inner regions of the atom to ones with lesser (i.e., from $l=0$ to $l=l_{\max}=n_0-1$, for fixed n_0). The DF potential energies are dominated by the nuclear and Hartree (or tadpole) contributions. Exchange effects decrease with increasing nuclear charge (for neutral atoms). They decrease even more rapidly as one goes from inner- to outer-shell electrons of the same atom. The correlation contributions to the energy can be understood in terms of a combination of overlap effects (as typified by the exchange contribution) and classical electrostatic arguments (that the potential of a charged sphere at a given radius should depend on the charge enclosed within that radius). The relativistic effects studied, FS and Breit contributions, also have the orders of magnitude that one would expect. All of these results give one some confidence that the estimates for the other effects given in Ref. 14, particularly for the QED effects, are also reasonable. Indeed, there is some evidence from the literature[20,21] for the qualitative behavior of the Lamb shift being of order $\alpha^3 Z_{\text{eff}}^2$ relative to the DF energies,[14] but information on the many-electron atoms of interest to us in this work awaits consideration. There are also QED corrections to *e*-*e* interactions which have recently been exhibited.[14] These remain to be calculated as well. It appears that the evaluation of the finite contributions due to these corrections can be carried out,[22] using a generalization of the procedure of Erickson and Yennie.[23]

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[18] The assumption of a virial theorem for $1/r$ potentials can actually be tested. We find that it is quite accurate for deep core and far valence states. It is not as accurate for levels in between. Our qualitative estimates are meant to indicate orders of magnitude only, and thus such errors are acceptable.

[19] Equation (29) is Eq. (52) of Ref. 7. We must bear in mind that, in using Eq. (36) of this reference, the term with P_{12} in it dominates over 1 in $(1-P_{12})$, if we use our arguments above about overlap.

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