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Relativistic Independent-Particle Model for Atoms, Based on Analytical Potentials*

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A two-parameter analytic potential for electrons in atoms, introduced by Green, Sellin, and Zachor, is used in conjunction with Dirac's equation to determine independent-particle-model electronic energy levels for neutral atoms in their ground states. The parameters are determined for each atom so that the predicted energy levels approximate observed electronic separation energies in accordance with a weighted least-squares sum. The agreement with experimental data is as good as for relativistic Hartree-Fock results. Electronic energies are given for a random selection of elements with $Z = 10, 20, \dots, 90$.

In a recent study, Green, Sellin, and Zachor¹ used a simple analytical potential to treat bound states of electrons in an atom in the nonrelativistic independent-particle-model approximation. For an atom containing N electrons and Z nuclear protons, their potential is of the form

$$V(r) = 2[(N-1)\mathcal{T}(r) - Z]/r, \quad (1)$$

$$\mathcal{T}(r) = 1 - 1/[e^{r/d} - 1]H + 1]. \quad (2)$$

It was shown that the parameters d and H can be suitably adjusted for each atom to reproduce approximately observed or calculated electronic energies for neutral atoms in their ground states.

Such analytical potentials are clearly much more convenient for many applications, such as the calculation of scattering cross sections or transition probabilities, than numerically generated ones such as those obtained from Hartree-Fock-Slater calculations. This is particularly the case when computations for very many atoms are being undertaken. Furthermore, as we shall demonstrate, the electronic energies obtained from the potential (1) are certainly not in worse agreement with experimentally determined values (insofar as the latter can be identified) than results of Hartree-Fock and related calculations.

The Green-Sellin-Zachor work has the drawback that the electrons are treated nonrelativistically. This, as is known, leads to poor results for inner-core electrons, particularly for heavy elements. Though the relativistic correction, and spin-orbit splitting, can be accounted for by adding suitable terms to the nonrelativistic Hamiltonian, one

might as well use the Dirac equation in place of the Schrödinger equation. This has been done in the present work, thus permitting direct comparison with experimental data or relativistic Hartree-Fock calculations.

The Dirac equation for an electron moving in a spherically symmetrical potential $V(r)$ is

$$[c\vec{\alpha} \cdot \vec{p} + \beta mc^2 + V(r)]\psi = E\psi, \quad (3)$$

where all the symbols have their usual meaning.² As is well known, the equation can be reduced to radial form in this case:

$$dF/dr = -(K/r)F + \frac{1}{2}\alpha[\epsilon - V(r) + 4/\alpha^2]G, \quad (4)$$

$$dG/dr = (K/r)G - \frac{1}{2}\alpha[\epsilon - V(r)]F, \quad (5)$$

where $F = F_{n1j}(r)$ and $G = G_{n1j}(r)$ are the large and small radial components, respectively. Here, $\epsilon = E - mc^2$, $\alpha = e^2/\hbar c$, $K = (l-j)(2j+1)$ while n , l , and $j = l \pm \frac{1}{2}$ are the usual principal orbital-angular-momentum and total-angular-momentum quantum numbers. We use rydberg units, $2m = \hbar = \frac{1}{2}e^2 = 1$, so that lengths are measured in units of Bohr radii and energies in units of $me^4/2\hbar^2 \approx 13.6$ eV.

In determining solutions of (4) and (5) numerically we used the second-order equation

$$d^2u/dr^2 + Qu = 0, \quad (6)$$

where

$$Q = -\frac{1}{4B} \frac{d^2V}{dr^2} - \frac{3}{16B^2} \left(\frac{dV}{dr} \right)^2 + \frac{K}{2Br} \frac{dV}{dr} + \frac{1}{2}\alpha^2 (\epsilon - V)B - \frac{K(K+1)}{r^2}$$

and

$$B = \frac{1}{2}[\epsilon - V + 4/\alpha^2],$$

which is obtained by eliminating G from (4) and (5) and setting $F = B^{1/2}u$. The form (6) is now amenable to numerical solution using the relatively efficient Numerov³ technique, the application of which to numerical solution of the radial Schrödinger equation is discussed in many places.^{4,5} In solving (6) numerically we have used, in essence, a modification of the Schrödinger-equation program described by Herman and Skillman.⁵

For each atom we determine the parameters H and d from the condition that the weighted least-squares sum

$$\chi(d, H) = \sum \frac{(E_{\text{obs}} - E_{\text{calc}})^2}{|E_{\text{obs}}^p|} \quad (7)$$

is minimized. The summation in (7) is taken over all electronic levels of the atom, E_{obs} are the desired electronic energies taken from experimental measurements of electronic energies⁶ or relativistic Hartree-Fock calculations,⁷ while E_{calc} are the energies predicted by the present model. When the weighting factors are given the power $p=2$, χ represents simply the sum of the squares of the fractional deviations from the desired energies, with all levels given equal weighting. Since our main purpose is to reproduce observed energies, which decrease in reliability with increasing electronic energy, we give greater weight to the inner electronic levels, by using the power $p=1$ in most determinations of d and H . Table I shows our results for $Z=40$ with d and H adjusted in three different ways. The first and third entries [columns labeled E (ESCA) and E (RHF)] are experimental⁶ and rela-

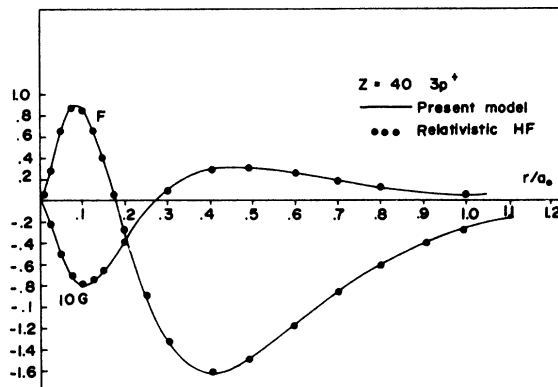


FIG. 1. Radial wave functions for $3p^+$ electrons of Zr ($Z=40$). Solid curve: present model using potential parameters of Table I (the curves for the three sets of parameters are indiscernible on this scale). Dots: relativistic Hartree-Fock results of Mann.⁷

tivistic Hartree-Fock⁷ results. The column labeled E_1 (GSZ) gives the energies computed from the present model with parameters adjusted to fit experimental energies with lower levels given greater weighting [i. e., $p=1$ in (7)]. The column labeled E_2 (GSZ) gives analogous results obtained by fitting to relativistic Hartree-Fock data, while E_3 (GSZ) corresponds to E_1 (GSZ) but with equal weighting of all levels [i. e., $p=2$ in (7)].

Note that either experimental or Hartree-Fock results can be approximated equally well, as evidenced by an inspection of the relative deviations

$$E_r = \left| \frac{E_{\text{calc}} - E_{\text{obs}}}{E_{\text{obs}}} \right|$$

TABLE I. Electronic energies for Zr ($Z=40$). E (ESCA), E (RHF), and E_i , $i=1, 2, 3$, are experimental,⁶ relativistic Hartree-Fock,⁷ and present-model results, respectively. $E_{r_i} = 100 |(E_i - E)/E|$, with $E = E$ (ESCA) for $i=1$ and $E = E$ (RHF) for $i=2, 3$.

	E (ESCA)	E_1 (GSZ)		E (RHF)	E_2 (GSZ)		E_3 (GSZ)	
		$d=0.80197$ $H=3.6429$	$p=1$		E_{r1}	$d=0.94932$ $H=4.2804$	$p=1$	E_{r2}
$1s^+$	1322.81	1324.31	0.11	1331.052	1327.18	0.29	1326.33	0.35
$2s^+$	186.10	184.28	0.97	189.690	187.06	1.38	186.75	1.55
$2p^-$	169.56	170.07	0.30	173.010	172.90	0.06	172.52	0.28
$2p^+$	163.39	163.52	0.08	166.644	166.34	0.18	165.97	0.40
$3s^+$	31.68	30.75	2.94	33.393	32.68	2.15	32.64	2.27
$3p^-$	25.36	25.16	0.79	27.068	27.11	0.14	27.06	0.03
$3p^+$	24.33	24.10	0.93	26.010	26.02	0.06	25.98	0.11
$3d^-$	13.45	13.77	2.39	14.918	15.76	5.66	15.72	5.37
$3d^+$	13.23	13.58	2.63	14.701	15.56	5.84	15.52	5.56
$4s^+$	3.82	3.79	0.88	5.019	4.63	7.69	4.66	7.23
$4p^-$	2.13	2.26	6.34	3.169	3.02	4.59	3.05	3.88
$4p^+$	2.13	2.13	0.07	2.911	2.87	1.52	2.89	0.75
$4d^-$	0.22	0.18	16.67	0.592	0.54	8.79	0.56	5.67
$5s^+$				0.429	0.49	14.82	0.50	16.41

listed in the columns labeled E_{r1} and E_{r2} . The energy values obtained are not very sensitive to the power of the weighting factors employed (cf.) E_{r1}

and E_{r3}) but the parameters d and H show substantial variation for the three computations exhibited. Figure 1 is a plot of the wave functions F and G

TABLE II. Electronic energies and potential parameters for a selection of atoms. The parameters were chosen so that results of present model approximate experimental values. The relativistic Hartree-Fock values are shown for purposes of comparison.

Z	d	H	$1s^+$	$2s^+$	$2p^-$	$2p^+$	$3s^+$	$3p^-$	$3p^+$	$3d^-$	$3d^+$	$4s^+$						
10 (Ne)	0.4272	1.0309	63.723	3.307	1.323		← Experimental results ⁶											
			63.695	3.050	1.381	1.373	← Present model											
			65.635	3.872	1.705	1.697	← Relativistic Hartree-Fock ⁷											
20 (Ca)	0.8800	2.9458	296.784	32.192	25.724	25.234	3.234	1.911										
			296.086	31.301	26.151	25.852	3.244	1.919	1.892	0.367								
			300.327	33.934	27.463	27.185	4.524	2.698	2.668	0.393								
30 (Zn)	0.5424	2.1173	709.916	87.757	76.732	75.041	10.069	6.394		0.661								
			712.915	86.216	77.128	75.241	9.601	6.453	6.227	0.705	0.682	0.589						
			715.497	90.692	79.480	77.702	11.600	7.916	7.674	1.542	1.509	0.597						
40 (Zr)	0.8020	3.6429	1322.81	186.10	169.56	163.39	31.68	25.36	24.33	13.45	13.23	3.82						
			1324.31	184.30	170.07	163.52	30.75	25.16	24.10	13.77	13.58	3.79						
			1331.05	189.69	173.01	166.64	33.39	27.07	26.01	14.92	14.70	5.02						
50 (Sn)	0.6137	2.8936	2146.12	328.17	305.46	288.77	64.97	55.64	52.55	36.31	35.64	10.07						
			2172.48	331.85	314.24	296.15	62.14	54.03	50.69	35.22	34.49	8.64						
			2158.64	332.62	309.76	292.73	67.11	57.74	54.53	38.16	37.51	11.76						
60 (Nd)	0.8743	4.5939	3202.23	523.75	494.05	456.28	115.83	103.12	95.40	73.50	71.88	23.23						
			3230.80	524.99	501.07	461.04	112.45	101.12	93.18	72.00	70.25	22.43						
			3220.82	529.08	499.23	460.89	118.25	105.50	97.61	75.72	73.94	25.03						
70 (Yb)	0.6284	3.5099	4507.78	770.85	733.36	657.29	176.17	159.64	143.25	115.83	112.22	35.79						
			4563.01	775.42	746.71	665.70	171.61	156.92	140.03	112.54	108.77	34.43						
			4535.36	777.79	740.11	662.97	179.42	162.84	146.19	118.38	114.78	37.35						
80 (Hg)	0.6201	3.6908	6107.90	1090.64	1044.33	902.85	261.80	241.00	209.25	175.29	168.68	58.80						
			6195.57	1101.05	1066.36	915.66	257.04	238.48	205.71	171.47	164.32	57.04						
			6148.65	1100.53	1053.70	910.31	266.23	245.28	213.08	178.86	172.03	61.30						
90 (Th)	0.9796	6.3349	8059.12	1504.65	1447.39	1198.02	380.87	355.07	297.37	256.58	244.90	97.75						
			8170.54	1512.17	1468.09	1204.52	374.29	350.63	291.80	249.47	237.36	96.27						
			8117.63	1517.21	1459.77	1207.15	386.23	360.25	301.77	260.60	248.69	100.37						
	$4p^-$	$4p^+$	$4d^-$	$4d^+$	$4f^-$	$4f^+$	$5s^+$	$5p^-$	$5p^+$	$5d^-$	$5d^+$	$6s^+$	$6p^-$	$6p^+$	$6d^-$	$6d^+$	$7s^+$	
	2.13		0.22															
	2.26	2.13	0.18				0.383											
	3.17	2.91	0.59				0.429											
	6.54		1.74	1.74			0.07	0.07										
	5.90	5.37	1.04	0.98			0.61	0.29										
	8.49	7.90	2.66	2.57			1.01	0.49										
	17.93	16.54	8.67	8.67	0.15		2.79	1.62										
	18.06	16.41	8.93	8.64	0.18		3.12	1.90	1.66				0.35					
	20.17	18.23	10.27	9.55	0.78		3.71	2.25	1.95				0.35					
	29.11	25.21	14.48	13.52	0.44		3.90	1.69										
	28.31	24.62	14.05	13.38	0.47	0.38	4.27	2.50	1.99									
	30.55	26.75	15.56	14.84	1.09	0.96	4.88	2.84	2.37				0.39					
	49.76	41.97	27.86	26.46	7.57	7.28	8.82	5.95	4.26	0.51								
	48.80	41.07	26.83	25.37	6.90	6.62	8.89	6.10	4.69	0.88	0.74	0.65						
	52.25	44.37	29.59	28.10	8.94	8.62	10.21	7.08	5.69	1.30	1.15	0.66						
	85.85	71.15	52.48	49.76	25.28	24.62	21.32	16.83	13.38	6.98	6.47	4.41	3.60	3.16	0.15			
	85.45	70.45	52.16	49.38	25.50	24.86	22.12	17.89	14.22	7.79	7.23	3.70	2.42	1.75	0.34	0.43		
	88.68	73.41	54.63	51.79	27.05	26.33	23.12	18.49	14.99	7.95	7.41	4.11	2.66	1.97	0.45	0.41		

for the $3p^*$ state of $Z=40$. Relativistic Hartree-Fock and present-model wave functions (using the parameters given in Table I) are exhibited. Clearly the agreement is very good. Results for other atoms are similar. Table II shows our results for a random selection of elements ($Z=10, 20, \dots, 90$). In each case the top entry is the experimentally determined value, the second entry is our fit to it [with $p=1$ in (7)], resulting in the parameters indicated on the left, while the bottom entries are relativistic Hartree-Fock energies shown for purposes of comparison. The numerical (FORTRAN IV) programs used to obtain these results are available on request.

The results presented above indicate that a simple analytical potential can yield as good a description of ground-state atoms as a numerically generated one from self-consistent field methods. For application purposes, the former has obvious advantages. It is evident, in particular, that the two-parameter analytical potential of Green, Sellin, and Zachor serves as well for relativistic calculations as it did for the nonrelativistic independent-particle-model work.

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Spin-Exchange Effects on Density-Matrix Elements*

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The work of Balling, Hanson, and Pipkin on the density-matrix equations for spin-exchange collisions is extended and is simplified in the case of $^2S_{1/2}$ atoms. The results allow straightforward calculation of the detailed effects of spin exchange on the density-matrix elements. The equations are useful when dealing with an ensemble of atoms such as in the hydrogen maser, in the rubidium maser, and in optical pumping cells.

I. INTRODUCTION

Spin exchange^{1,2} is one of the dominant mechanisms effecting changes in the spin states of colliding atoms having unpaired electrons. For an ensemble of atoms, the characterization of the spin coordinates can be conveniently made by a density matrix. The effect of spin exchange on the elements of this density matrix is an important consideration when dealing with systems of colliding atoms, such as in the hydrogen maser,³ in the rubidium maser,⁴ or in optical pumping cells.⁵

The result of exchange of electron spin coordinates can be derived by considering elastic scattering from a spin-dependent potential. Balling, Hanson, and Pipkin (BHP)⁵ have used this method to calcu-

late the effect of spin exchange on the density matrix. Their theory ignores spin-orbit interactions and direct magnetic interactions between the colliding atoms. As shown below, a simplification of their result can be made in the case of spin exchange between $^2S_{1/2}$ atoms, wherein the effect of spin exchange on the density matrix of each system is only through the electron polarization of the other, and is not dependent on the specific population of each hyperfine level.

II. DENSITY MATRIX RATE EQUATION

Consider the two-body collision involving an atom of type A and an atom of type H . (A may be the same as or different from H .) The joint density matrix for this composite system is