

Independent-particle-model potentials for ions and neutral atoms with $Z \leq 18$

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The atomic independent-particle model of Green, Sellin, and Zachor (GSZ) is used to obtain potentials for electrons in ions of light elements ($Z \leq 18$). The two parameters of such potentials are obtained by the *ab initio* procedure of Bass, Green, and Wood (BGW). Here the expectation of the exact Hamiltonian with respect to a Slater determinant of one-electron wave functions corresponding to GSZ potentials is minimized. Total energies determined by this modified Hartree-Fock procedure are found to be in excellent agreement with Hartree-Fock values (usually within a hundred parts per million). Potential parameters obtained in this way are found to be strongly dependent on both the atomic number and the number of electrons in the ion. Several other simple analytic potentials are treated in a similar way and it is found that the two-parameter GSZ and Gaspar potentials yield energies substantially lower than one-parameter potentials of the forms used earlier by Bohr and Tietz.

I. INTRODUCTION

Theoretical investigations of atomic systems are usually based on some version of the Hartree-Fock self-consistent field model in which each electron is assumed to move in a potential produced by the others. True Hartree-Fock calculations are complicated by the fact that the potential is nonlocal. Even local approximations to the exchange term in the potential, such as the Hartree-Fock-Slater (HFS) approximation,¹ still require an iterative procedure to obtain the potential which must be generated numerically and then must be tabulated point by point as a function of the electron's position from the nucleus. Additionally, the HFS potential falls off too rapidly and to correct for this it is customary, following Latter,² to impose a Coulomb tail to approximate the hydrogenlike behavior of the potential at large distances. This device introduces a discontinuity in the derivative of the HFS potential.

Calculations using an analytic independent-particle-model (IPM) potential offer a computationally convenient and accurate method for computing atomic wave functions. Particularly convenient is the ability to characterize such IPM potentials by a few parameters whose variation with such quantities as atomic number and ionicity can be illustrated in graphical form or represented by fits with appropriate functional forms.

Such parameters may be adjusted to experimental data or to the results of more complex computations to provide a realistic single-particle description of a complex many-body system. A single IPM potential can often give an accurate description of single-electron wave functions for unoccupied as well as occupied orbitals. The orthogonality and closure properties of such an IPM are particularly useful in calculating the properties of

excited electronic states and states in the continuum in addition to those of the occupied orbitals of the ground state. Moreover, in applied work, for which we are computing the relevant atomic data, phenomenological adjustment of the potential parameters allows for small effects, such as attractive core polarization, which are extremely difficult to treat in a more rigorous way.

The analytic independent-particle model of Green, Sellin, and Zachor³ (GSZ) has proven particularly successful in computing atomic properties. The GSZ potential for neutral atoms has the form

$$V(r) = -(2/r)[(Z-1)\Omega(r)+1], \quad (1)$$

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

where r is the radial distance from the nucleus, Z is the nuclear charge, and H and d are adjustable parameters. Single-particle wave functions resulting from calculations with the GSZ potential have been used effectively to compute one-electron energies for occupied orbits,³ electron-elastic-scattering cross sections,⁴⁻⁶ and electron excitation and ionization cross sections⁷⁻¹⁰. Results obtained using GSZ-IPM wave functions for computing inner-shell ionization processes¹¹ and optical oscillator strengths¹² compare favorably with those obtained using HFS wave functions. Variations of this same model have been used to compute the energy levels of diatomic molecules,¹³ to compute the cross sections for elastic scattering of electrons by molecules,¹⁴ and to provide the foundation for determining atom-atom and ion-atom scattering potentials.¹⁵

Recently, Hahn and Watson¹⁶ used wave functions obtained by solving the Schrödinger equation for the GSZ potential to calculate transition probabilities to bound and continuum states of atoms and

highly charged ions. In their work the same d parameter was used for ions as for the respective neutral atoms and H was assumed to vary as

$$H = (Z - \eta)^{0.4} d, \quad (3)$$

where η is the degree of ionicity plus one, which is a generalization of an equation for neutral atoms proposed by GSZ. The investigation reported here was stimulated in part by the desire to establish whether these simple rules for the d and H parameters of ionized atoms are the best that can be found. In a broader measure, however, the purpose of this work is to extend the GSZ independent-particle model to positive and negative ions by obtaining potential parameters suitable for their description.

In extending the model to ions it would be preferable to use an *ab initio* method of determining the potential parameters rather than use a phenomenological adjustment to experimental data or the results of a previous more rigorous calculation. The modified Hartree-Fock approach of Bass, Green, and Wood¹⁷ is an example of such a method. Here the expectation of the total Hamiltonian of an atom or ion, whose one-electron wave functions are eigenfunctions of the IPM potential, is minimized with respect to the potential parameters. As one indicator of the accuracy of such an approach, total energies obtained using this criterion usually differ from Hartree-Fock values by less than one hundred parts per million. With this condition on the total energy the single-electron eigenvalues are not in as precise agreement with Hartree-Fock values as they would be if a phenomenological fit were performed. However, the accuracy is still about the same as that obtained with the HFS- $X\alpha$ method. The present work extends the study of Bass, Green, and Wood to encompass ionized atoms.

II. THEORY

One-electron wave functions of the atom are assumed to have the form

$$U_{nlmi}(\vec{r}, s) = r^{-1} P_{nl}(r) Y_{lm}(\theta, \varphi) \Gamma_i(s), \quad (4)$$

where n is the principal quantum number, l the orbital angular momentum, m the magnetic quantum number, and $\Gamma_i(s)$ the spin eigenfunction. These functions are constrained to satisfy the eigenvalue equation

$$[-\nabla^2 + V(r)] U_{nlmi}(\vec{r}, s) = E_{nl} U_{nlmi}(\vec{r}, s), \quad (5)$$

where $V(r)$ is the GSZ potential modified for ions, using the form

$$V(r) = -(2/r)[(Z - \eta)\Omega(r) + \eta], \quad (6)$$

and $\Omega(r)$ is given by Eq. (2). The total Hamiltonian is taken as

$$H = \sum_i \left(\frac{p_i^2}{2m} - \frac{2Z}{r_i} \right) + \sum_{i>j} \frac{2}{|r_i - r_j|}. \quad (7)$$

The expectation value of this Hamiltonian, i.e., the total energy, averaged over all Slater determinants which can be constructed from a given configuration, is¹⁸

$$\bar{E} = \sum_{nl} W_{nl} \left(I_{nl} + \frac{1}{2} \sum_{n'l'} (W_{n'l'} - \delta_{nl;n'l'}) M_{nl;n'l'} \right), \quad (8)$$

where W_{nl} is the number of electrons in the nl shell,

$$I_{nl} = \int_0^\infty P_{nl}(r) \left(-\frac{d^2}{dr^2} - \frac{2Z}{r} + \frac{l(l+1)}{r^2} \right) P_{nl}(r) dr, \quad (9)$$

$$\delta_{nl;n'l'} = 1 \quad \text{if } n=n' \text{ and } l=l',$$

$$\delta_{nl;n'l'} = 0 \quad \text{otherwise.}$$

$$M_{nl;nl} = F_{nl;nl}^0 - (4l+1)^{-1} \sum_{k=1}^{\infty} c^k(l0; l0) F_{nl;nl}^k, \quad (10)$$

$$M_{nl;n'l'} = F_{nl;n'l'}^0 - \frac{[(2l+1)(2l'+1)]^{1/2}}{2} \times \sum_{k=0}^{\infty} c^k(l0; l'0) G_{nl;n'l'}^k, \quad n \neq n' \text{ or } l \neq l',$$

with

$$F_{nl;n'l'}^k = 2 \int_0^\infty \int_0^\infty P_{nl}(r_1) P_{n'l'}(r_2) \times \frac{r_<^k}{r_>^{k+1}} P_{nl}(r_1) P_{n'l'}(r_2) dr_1 dr_2, \quad (11)$$

$$G_{nl;n'l'}^k = 2 \int_0^\infty \int_0^\infty P_{nl}(r_1) P_{n'l'}(r_2) \times \frac{r_<^k}{r_>^{k+1}} P_{nl}(r_2) P_{n'l'}(r_1) dr_1 dr_2,$$

where

$$r_< = \text{smaller of } (r_1, r_2), \quad (12)$$

$$r_> = \text{larger of } (r_1, r_2).$$

The $c^k(lm; l'm')$ are coefficients resulting from the angular integrations and are tabulated in Appendix 20 of Ref. 18.

With the assumption that the $P_{nl}(r)$ satisfy the radial differential equation

$$\left(-\frac{d^2}{dr^2} + V(r) + \frac{l(l+1)}{r^2} \right) P_{nl}(r) = E_{nl} P_{nl}(r), \quad (13)$$

derived from Eq. (5), the variational problem of \bar{E} with respect to the $P_{nl}(r)$ becomes a variational

problem with respect to the parameters d and H of the potential $V(r)$. Thus we obtain a first-principles estimate of these parameters for a potential of the form given by Eqs. (2) and (6).

III. CALCULATIONAL METHODS

For all elements with $Z \leq 10$ plus silicon ($Z=14$) and argon ($Z=18$), the total energies of the neutral atoms, of all positive ions (short of the hydrogenic ions), and, where possible, of the negative ions were computed and minimized with respect to $K(=H/d)$ and d . Our purpose was to take advantage of the observation of GSZ and BGW which indicated that K for neutral atoms is a smoothly varying function of Z , whereas the parameter H shows the same strong dependence on the atomic shell structure as d .

The minimization procedure used was a variation of the "brute-force" method of Roothaan and Bagus.¹⁹ No procedures were incorporated for accelerating or refining the approach to an energy minimum. Holding one parameter fixed, the second was varied at specified intervals until the total energy [\bar{E} of Eq. (8)] passed through a minimum and began to increase. The value of \bar{E} at five points was fitted with a fourth-degree polynomial and the coefficients of the polynomial were then used to compute the value of the parameter at which the \bar{E} was a minimum. The program incremented the second parameter by a specified amount, and the first parameter was once more varied in the vicinity of the previous one-parameter minimum by the method indicated above. When the program sensed that the two-dimensional parameter space included the energy minimum, a quadratic fit was performed to the energy surface and the parameters of the energy minimum were computed from this fit.

The minimum total energies obtained via these procedures were compared to the Hartree-Fock results of Clementi²⁰ or Mann,²¹ with the exception of the Hartree-Fock energy of the negative hydrogen ion, which was obtained from the calculation of Dutta *et al.*²²

The independent-particle model in the form applied here cannot distinguish among the various terms of a multiplet. Thus, in comparing the IPM to Hartree-Fock results, the latter are taken as weighted energies of the form

$$E = \frac{\sum_S \sum_L (2S+1)(2L+1)E_{LS}}{\sum_S \sum_L (2S+L)(2L+1)}, \quad (14)$$

where E_{LS} are total energies of states with the same electronic configuration as the ground state but with different values of total orbital angular momentum L and total spin S .

IV. OTHER ANALYTIC POTENTIALS

Having developed the machinery for this modified Hartree-Fock technique we take the occasion of this study to examine a number of other simple analytic potentials. Our purpose is to obtain a physical indication of the sensitivity of the results to the form of the potential, which here depends upon the choice of screening function. In particular we will study a simple one-parameter (P_1) exponential screening function

$$\Omega(r) = e^{-P_1 r}, \quad (15)$$

which corresponds to the Bohr, Debye, or Yukawa potential. We have also examined the screening function of Tietz,²³

$$\Omega(r) = \frac{1}{(1 + P_1 r)^2}, \quad (16)$$

as well as the two-parameter (P_1 and P_2) screening function of Gaspar,²⁴

$$\Omega(r) = \frac{e^{-P_1 r}}{1 + P_2 r}. \quad (17)$$

The parameters in these screening functions have been adjusted to the Thomas-Fermi screening function. However, in applications Gaspar actually solved the Schrödinger equation with the corresponding potential form. With the resulting wave functions he computed quite successfully the x-ray spectra of several intermediate and heavy atoms.

V. RESULTS AND DISCUSSION

A. GSZ potential parameters

The parameters d and K of the GSZ potential which produce the minimum total energy for a particular ion are listed in Table I together with the deviations of these energies from Hartree-Fock results. Negative ions absent from the table consist of a single electron outside of filled orbitals. It was not found possible to bind this electron with any reasonable choice of potential parameters, i.e., within a rather large space around those which minimized the energy of the neutral and taking due account of trends in the parameter with atomic number and the number of electrons.

The quantity δ , which is always positive, is defined by

$$\delta = \frac{E_{\text{IPM}} - E_{\text{HF}}}{E_{\text{HF}}} \quad (18)$$

and is given in parts per million. E_{IPM} and E_{HF} are, respectively, the total energies obtained from independent-particle-model and Hartree-Fock calculations. Deviation from Hartree-Fock results of the total energies of positive ions computed

TABLE I. GSZ potential parameters producing minimum total energy and deviations of these total energies from Hartree-Fock results.

Electronic configuration	Ion or atom	d (a.u.)	K (a.u.)	δ (ppm)	Electronic configuration	Ion or atom	d (a.u.)	K (a.u.)	δ (ppm)	
$1s^2$	H ⁻	1.107	0.744	405	$1s^2 2s^2 2p^2$	Ne ⁴⁺	0.326	3.92	38	
	He	0.381	1.77	0.5		Si ⁸⁺	0.200	5.67	18	
	Li ⁺	0.231	2.80	1.1		A ¹²⁺	0.145	7.50	11	
	Be ²⁺	0.176	3.93	3.0	$1s^2 2s^2 2p^3$	C ⁻	1.55	1.84	130	
	B ³⁺	0.140	5.05	1.5		N	0.848	2.27	94	
	C ⁴⁺	0.100	5.70	0.4		O ⁺	0.596	2.69	69	
	N ⁵⁺	0.096	7.15	0.2		F ²⁺	0.456	3.10	55	
	O ⁶⁺	0.080	8.10	0.1		Ne ³⁺	0.376	3.52	42	
	F ⁷⁺	0.066	8.80	0.1		Si ⁷⁺	0.216	5.15	19	
	Ne ⁸⁺	0.061	10.0	0.0		A ¹¹⁺	0.161	6.90	12	
	Si ¹²⁺	0.057	15.9	0.6	$1s^2 2s^2 2p^4$	N ⁻	1.17	2.00	86	
A ¹⁶⁺	0.042	20.1	0.7	O		0.735	2.41	65		
$1s^2 2s$	Li	0.462	1.75	240		F ⁺	0.542	2.82	50	
	Be ⁺	0.309	2.42	135		Ne ²⁺	0.432	3.22	40	
	B ²⁺	0.233	3.09	84	Si ⁶⁺	0.245	4.85	20		
	C ³⁺	0.190	3.77	58	A ¹⁰⁺	0.170	6.40	11		
	N ⁴⁺	0.152	4.41	42	$1s^2 2s^2 2p^5$	O ⁻	1.13	2.28	130	
	O ⁵⁺	0.135	5.11	32		F	0.663	2.59	50	
	F ⁶⁺	0.116	5.75	25		Ne ⁺	0.485	2.94	39	
	Ne ⁷⁺	0.100	6.36	20		Si ⁵⁺	0.252	4.44	20	
	Si ¹¹⁺	0.071	9.00	11		A ⁹⁺	0.170	5.92	12	
A ¹⁵⁺	0.060	12.0	6	$1s^2 2s^2 2p^6$	F ⁻	0.800	2.36	52		
$1s^2 2s^2$	Li ⁻	2.31	1.34		266	Ne	0.558	2.71	42	
	Be	0.769	1.88		113	Si ⁴⁺	0.270	4.17	20	
	B ⁺	0.490	2.41		68	A ⁸⁺	0.180	5.62	12	
	C ²⁺	0.360	2.96	47	$K(2)L(8)3s$	Na ^a	0.584	2.85	68	
	N ³⁺	0.296	3.52	34		Si ³⁺	0.336	3.88	38	
	O ⁴⁺	0.245	4.07	26		A ⁷⁺	0.220	5.28	22	
	F ⁵⁺	0.207	4.59	20		$K(2)L(8)3s^2$	Mg ^a	0.670	3.01	55
	Ne ⁶⁺	0.183	5.16	16	Si ²⁺		0.435	3.65	37	
	Si ¹⁰⁺	0.127	7.30	8	A ⁶⁺		0.274	4.98	23	
	A ¹⁴⁺	0.090	9.55	5	$K(2)L(8)3s^2 3p$	Al ^a	0.860	3.17	79	
$1s^2 2s^2 2p$	B	0.970	2.00	153		Si ⁺	0.628	3.46	52	
	C ⁺	0.613	2.48	98		A ⁵⁺	0.350	4.72	27	
	N ²⁺	0.456	2.96	67		$K(2)L(8)3s^2 3p^2$	Si	0.988	3.26	71
	O ³⁺	0.367	3.45	48			A ⁴⁺	0.428	4.42	30
	F ⁴⁺	0.307	3.94	36	$K(2)L(8)3s^2 3p^3$		Si ⁻	1.78	3.07	80
	Ne ⁵⁺	0.262	4.42	28		P ^a	1.055	3.33	57	
	Si ⁹⁺	0.170	6.40	15		A ³⁺	0.541	4.18	33	
	A ¹³⁺	0.114	8.11	9		$1s^2 2s^2 2p^2$	A ²⁺	0.670	3.92	32
B ⁻	1.96	1.65	169	$K(2)L(8)3s^2 3p^4$	A ⁺		0.835	3.71	32	
C	0.939	2.13	133							$K(2)L(8)3s^2 3p^5$
N ⁺	0.630	2.57	92							
O ²⁺	0.476	3.02	66							
F ³⁺	0.387	3.46	49	$K(2)L(8)3s^2 3p^6$						

^a From Ref. 17.

using the GSZ potential is generally equal to or less than that for the neutral atom. There is a slight increase in this deviation for the negative ions compared to that for the un-ionized atom. For fixed Z the accuracy generally increases as the number of electrons is decreased, but this trend is somewhat modulated by shell effects.

There is some tendency toward ambiguity in the choice of the parameters with increasing positive ionization. As electrons are removed the screening of the nuclear potential becomes smaller and the minima of the total energy surface in the two-parameter space become correspondingly broader.

The values of d and K which minimize the total energy are plotted in Figs. 1 and 2 as functions of atomic number for different numbers (n) of electrons. Both d and K exhibit considerable variation with both atomic number and the number of electrons. Because of the strong dependence of d on the atomic shell structure, no simple function can adequately represent its dependence on Z and n .

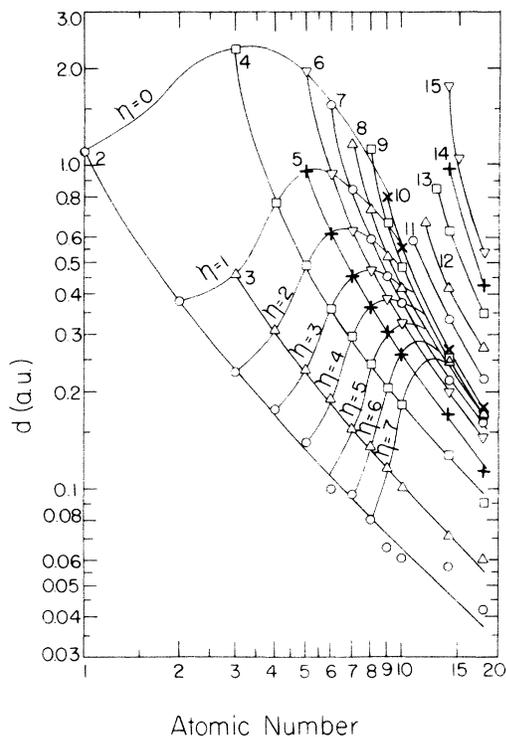


FIG. 1. Graphs of d parameters of the GSZ potential which produce minimum total energy for an ion or neutral atom as a function of Z . Except for $Z=14$, the values of d for neutral atoms with $Z>10$ are taken from Ref. 14. Smooth curves are best fits of Eq. (19) to the calculated points. The number next to each curve is the total number (n) of electrons in the ion or neutral atom. Contours of constant η are sketched in for values from 0 to 7.

However, for a fixed number of electrons d varies with Z approximately in accord with

$$d = d_n [\beta / (Z - Z_n + \beta)]^m, \quad (19)$$

where d_n is the scaling parameter for the neutral species Z_n and β and m are adjustable parameters

The K parameter is more regular and may be expressed approximately by the formula

$$K = K_n (Z/Z_n)^{1+\Delta}, \quad (20)$$

where Δ is a small parameter. While because of time and computer costs our work has been limited to the light elements, one might reasonably use Eq. (19) in conjunction with the results for d_n and K_n found by Bass *et al.* to extend the present work. Table II gives the values of β , m , and Δ which give the best fits to Eqs. (19) and (20) over the limited range of Z and n investigated here. For large Z and a small n , the d parameter deviates considerably from the smooth curve. Nevertheless, the actual accuracy of the total energy would be little affected (a few ppm at most) by using the parameters of the smooth curves because of the insensitivity mentioned previously.

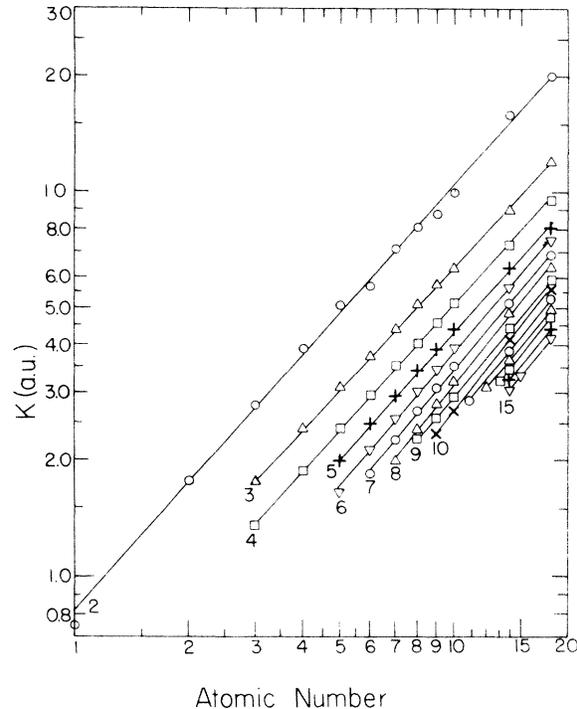


FIG. 2. Graphs of the K parameter of the GSZ potential which produces minimum total energy for an ion or neutral atom as a function of Z . The number at the bottom of each curve is the total number (n) of electrons in the ion or neutral atom.

TABLE II. Parameters β , m , and Δ , which produce best fits to the d -vs- Z and K -vs- Z curves using Eqs. (19) and (20).

n or Z_n	Parameter		
	β	m	Δ
2	1.48	0.944	0.105
3	1.93	0.972	0.078
4	1.38	0.857	0.093
5	1.77	0.984	0.121
6	1.81	0.913	0.163
7	2.06	0.910	0.189
8	2.48	0.901	0.227
9	2.06	0.798	0.198
10	2.90	0.848	0.252
11	3.38	0.870	0.257
12	2.42	0.717	0.243
13	1.48	0.609	0.221
14	1.5 ^a	0.644 ^a	0.211
15	1.92	0.710	0.238

^a Estimated in part from trends at other Z_n .

B. Total energy minima from other analytic potentials

The parameters of various potentials which produce minimum total energy for neon in different states of ionization are illustrated in Table III together with the deviations of these energies from Hartree-Fock results. The advantages of a two-parameter potential over a one-parameter potential in this context are obvious. The Gaspar form of the screening function gives results comparable to the GSZ form for carbon and xenon (also shown in Table III) as well as for the ions of neon. While difficulty might be expected with the Gaspar potential if P_2 became negative, this did not occur in the calculations performed here. For neon the optimum value of P_2 decreased abruptly from

positive values ~ 1 to zero (reducing the potential to a simple exponential form) when the 2s and 1s were the only occupied orbitals.

C. Other energy-related quantities computed from GSZ independent-particle model

While the accuracy with which the total energy can be computed is not to be denied, this is obviously only one indicator of the over-all accuracy of the computations presented here. A more complete analysis would require extensive computations with the wave functions resulting from the study such as were performed with the phenomenologically parametrized model described in the Introduction. The primary intent of the present investigation was to provide some justification for the *ab initio* prescription used to select the GSZ potential parameters. Nevertheless, it may be illuminating to look briefly at the accuracy with which energy-related quantities other than the total energy are computed. The ions of argon will be used for specific numerical examples.

One indication of the individual accuracy with which the kinetic energy and interaction energy are computed is given by the degree to which the virial theorem for atoms (total energy = - kinetic energy) is satisfied. In minimizing the total energy, true Hartree-Fock computations should automatically fulfill the requirements of the virial theorem¹⁸ and in actual practice this is verified to within a few parts per million.²⁰ In the present calculation the virial theorem is satisfied to within a few parts per thousand, with accuracy increasing with the degree of positive ionization. This is comparable to that obtained in HFS and HFS- $X\alpha$ ²⁵ computations. For the specific case of Ar^+ the virial theorem was fulfilled to within 0.3% for the

TABLE III. Parameters of various IPM potentials which produce minimum total energy and deviation of these energies from Hartree-Fock values.

Atom or ion	One-parameter potentials				Two-parameter potentials					
	Exponential		Tietz		GSZ		Gaspar			
	P_1 (a.u.)	δ (ppm)	P_1 (a.u.)	δ (ppm)	d (a.u.)	K (a.u.)	δ (ppm)	P_1 (a.u.)	P_2 (a.u.)	δ (ppm)
Ne	2.39	368	1.46	292	0.558	2.71	41	1.23	1.45	38
Ne ⁺	2.64	207	1.61	437	0.485	2.94	39	1.41	1.52	33
Ne ²⁺	2.91	137	1.77	209	0.432	3.22	40	1.66	1.52	35
Ne ³⁺	3.22	95	1.95	186	0.376	3.52	42	2.06	1.38	41
Ne ⁴⁺	3.64	64	2.18	167	0.326	3.92	38	2.57	1.23	39
Ne ⁵⁺	4.21	36	2.49	146	0.262	4.42	28	3.10	1.28	28
Ne ⁶⁺	5.22	16	2.95	126	0.183	5.16	16	5.22	0	16
Ne ⁷⁺	7.01	31	3.82	111	0.100	6.36	20	7.01	0	31
Ne ⁸⁺	11.5	2	6.50	11	0.061	10.0	0	11.5	0	2
C	0.939	2.13	133	0.673	1.43	122
Xe	0.955	5.10	30	0.520	4.62	43

TABLE IV. Single-electron eigenvalues of Ar⁺ computed from various atomic models.

Quantum numbers	Single-electron energies (Ry)			
	GSZ independent-particle model	Hartree-Fock	Hartree-Fock-Slater	HFS-X α
1s	-228.9	-238.3	-233.7	-229.4
2s	-23.1	-25.7	-24.0	-22.6
3s	-3.08	-3.42	-3.06	-2.58
2p	-18.4	-20.2	-19.3	-17.8
3p	-2.04	-2.09	-1.97	-1.53
3d	-0.68	-0.23

independent-particle model, to within 2.2% for the HFS model, and to within 0.7% for the HFS-X α method when α was set to $\frac{2}{3}$. Table IV shows that in computing single-electron eigenvalues (including that of the unoccupied 3d orbital) the IPM is competitive with HFS calculations. Both Table V, which compares the Ar⁺ experimental ionization potential with various computations, and Table VI, comparing the experimental and calculated energy of the "first" excited state of Ar⁺, also confirm the reliability of the IPM. For the latter comparison it was assumed that the experimental excited state was ²D, $J = \frac{5}{2}$ resulting from a transition 3p → 3d without spin flip from the ²P, $J = \frac{3}{2}$ ground state of Ar⁺. It is interesting to note that the energy difference of the 3p and 3d orbitals (1.36 Ry), computed from the parameters which minimize the ground-state energy, gives a fairly accurate estimate of the energy of the same excited state.

Ganas and Green¹² have given particular attention to a comparison of HFS and two IPM screening functions for atomic nitrogen in the neighborhood of the atom's "surface." They show that the HFS potential is particularly limited with respect to its ability to deal with low-lying excited states. This is true despite the use of the Latter² technique of replacing the HFS potential by $-2/r$ at radii where the absolute magnitude of the HFS potential becomes smaller than the Coulombic potential. Essentially this Latter device not only intro-

duces a discontinuity in the first derivative of the electron-atom potential, but it still leaves the HFS potential too small in absolute magnitude. Thus in the important region of potential which acts upon the active electron in its ground state and low-lying excited states, the HFS-HS screening function is considerably weaker than the analytic IPM screening functions with parameters obtained by two procedures. The analytic IPM function, obtained by adjustment to experimental separation energies, is strongest in this region and yields very precise excitation energies. The analytic potential obtained by the modified Hartree-Fock method used here is not quite as strong, but nevertheless considerably stronger than the HFS potential. It would appear that the adjustment-to-separation-energies procedure empirically incorporates a small attractive electron-core polarization potential, which is not included in the present procedure. Core polarization is not included in the HFS approximation, which also has additional deficiencies in this region despite the use of the Latter device. Because the ground-state HFS potential is not accurate for calculating single-electron wave functions for the unoccupied orbitals, the excited-state potentials are sometimes generated separately from that of the ground state. Unfortunately, this has the disadvantage of the concomitant nonorthogonality of the ground-state and excited-state wave functions.

TABLE V. Comparison of the experimental ionization potential of Ar⁺ and that computed from various atomic models.

Atomic model	Ionization potential (eV)
Experiment ^a	27.62
GSZ independent-particle model	27.41
Hartree-Fock	27.42
HFS-X α	27.14

^aC. E. Moore, *Atomic Energy Levels*, Natl. Bur. Std. (U.S.) Circ. No. 467 (U.S. GPO, Washington, D. C., 1949), Vol. I.

D. Efficiency and convenience of computational methods

In attempting to assess the inherent speed and efficiency of IPM calculations compared to those of other models, it is necessary to try to separate the attributes of the model from those of the computer programs and numerical techniques employed. The computer programs used for the IPM calculations were attached to the Hermann-Skillman program and utilized the brute-force minimization scheme described in Sec. III, requiring at least 25 computations of the total energy. Such quantities as the charge density and the SCF potential, though not germane to the IPM calculation, were still computed. An additional measure of uncertainty is introduced by the fact that the speed of completion of all those computations is a function of the accuracy of initial guesses. For the IPM the starting parameters of the potential are estimated. For Hartree-Fock-type computations it is the initial charge density.

Calculations for Ar^+ utilizing the three models, IPM, HFS, and HFS- $X\alpha$, are now compared. Using a convergence criterion of 10^{-7} on the single-electron eigenvalues and varying the GSZ potential parameters by increments $\sim 1\%$, the IPM could determine the energy minimum to better than 1 ppm. This sensitivity was further verified by repeating the calculation in the vicinity of this minimum using finer steps (\sim few tenths of one percent) in the GSZ potential parameters. The HFS calculation had not yet converged on the charge density in twice the time required to complete the IPM calculation. The HFS calculation used part of the same computational machinery as the IPM calculations and the same number of points in computing the wave function, started with an analytic fit to the Thomas-Fermi charge distribution, made use of the Hartree-Switendick²⁶ scheme to accelerate convergence of the charge distribution, and required convergence criteria of 10^{-5} on the charge distribution and 10^{-7} on the energy eigenvalue, the same as built into the HFS- $X\alpha$ computation described below.

The separate HFS- $X\alpha$ computer program proved

to be two to three times more efficient than the IPM computation. The HFS- $X\alpha$ calculation began with a rational approximation to the Thomas-Fermi charge density, used the Pratt²⁷ improvement scheme to accelerate convergence, required the same convergence criteria as the HFS computation, and was able to utilize a smaller number of optimally spaced mesh points in computing the wave function, with no apparent loss of accuracy. The number of mesh points used here was 251, whereas the IPM calculation failed if less than 441 were used.

The intrinsic efficiency of the IPM calculations has been overshadowed by improvident algorithms and numerical techniques. To remedy this, future IPM calculations of the type described here will use more efficient minimization procedures (such as the variable-metric-minimization method of Davidson²⁸ or the simplex method of Nelder and Mead²⁹), extraneous computations will be avoided, and a smaller mesh (such as that used in the HFS- $X\alpha$ code) incorporated into our calculations.

VI. CONCLUSIONS

Minimization of the total energy of a positive or negative ion provides an *ab initio* method for selecting the parameters of the GSZ independent-particle-model potential. The accuracy compared to Hartree-Fock values of total energies of ions computed via this procedure is of the same order as that obtained previously for neutral atoms. While a thorough survey of the computations of quantities other than the total energy has not been performed, it appears that potentials derived from such minimization procedures can calculate single-electron energies, ionization potentials, and excited-state energies with an accuracy at least equal to that of HFS computations.

Parameters which accomplish minimization of the total energy are rapidly varying functions of both the atomic number and the degree of ionization (or the number of electrons). These optimum parameters can, with reasonable accuracy, be characterized by simple equations [Eqs. (19) and (20)] in terms of a few parameters which have

TABLE VI. Comparison of the experimental energy of the "first" excited state of Ar^+ with that computed from two atomic models.

Atomic model	Excited-state energy (Ry)
Experiment ^a	1.377
GSZ independent-particle model	1.389
HFS- $X\alpha$	1.340

^a C. E. Moore, Ref. (a) in Table V, for further description of the experimental level chosen for comparison.

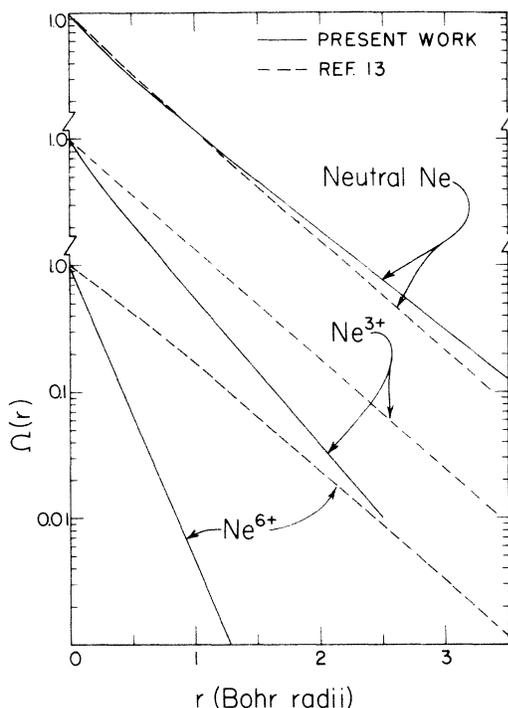


FIG. 3. Comparison of the screening function $\Omega(r)$ for neutral Ne, Ne^{3+} , and Ne^{6+} using the parameters of the present work and those of Ref. 16.

limited variation but which fluctuate with atomic shell structure. Some of these fluctuations may be due to ambiguities in the determination of the potential parameters. Such ambiguities might be resolved if an additional constraint on the selection of the potential parameters, such as choosing those which best satisfy the virial theorem, were also imposed.

Perhaps one of the main advantages of the analytic IPM model vis-à-vis numerical HFS or HFS- $X\alpha$ potentials is in the convenience of communication of results once the self-consistent parameters have been determined. For example, Hermann and Skillman list their final self-consistent screening functions for any element at 60–80 scaled radial coordinates for each neutral series. Using an analytic IPM we simply give two numbers per species to provide the user with at least as good an IPM screening function. If, as in this paper, we venture into the second dimension of ionicity, then the disadvantages of the HFS

procedure become even more obvious, particularly when the analytic IPM is used in conjunction with rules such as Eqs. (19) and (20). For example, for the $1s^2$ configuration, five numbers—the parameters d_n , K_n , β , m , and Δ as given in Tables I and II—suffice to determine good screening functions which in the HFS-HS methodology would require the transmittal of over 1000 numbers.

It should be noted that Eqs. (19) and (20) differ quite markedly from the rules used by Hahn and Watson (HW) in their survey of transition probabilities and multiple ionizations by high-energy electron impact. In effect, they use the rules $d = d_n$ and $K = n^{0.4}$. Figure 3 illustrates the differences in some of the screening functions implied by the differences in the two sets of rules. The figure suggests that the HW potentials fall off too slowly with distance and hence that their electrons would be too tightly bound. Accordingly, it would be interesting to refine their pioneering survey by examining the quantitative implications of our more physically based rules.

During the course of this study we have established that two-parameter potentials such as the GSZ and that of Gaspar yield total energies which are significantly more accurate relative to Hartree-Fock calculations than the one-parameter potentials of Bohr and Tietz.

Future work employing this minimization prescription will use more efficient computer techniques in order to take full advantage of the innate efficiency of calculations with the independent-particle model. In view of the past success of the GSZ IPM in characterizing the heavier neutral atoms, coupled with its current success with many light ions, there seems little question of the applicability of the model and our minimization procedures to heavier ions as well.

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