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Ab initio local-density potential for atoms: The modified Ξ method

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In the Ξ method, the self-interaction part of the total exchange-correlation potential in atoms is evaluated exactly and the remaining "pure exchange" is approximated using a Fermi-hole formalism. A theoretical derivation of an *ab initio* exchange potential for atoms using a simple model of this pure exchange hole is presented. This model of the exchange hole satisfies, unlike an earlier treatment, the necessary condition that the total charge removed from the exchange hole is zero. The orbital eigenvalues and the total energies of the ground-state multiplets for various atoms and ions are reported and found to be in close agreement with the Hartree-Fock values.

I. INTRODUCTION

The total exchange-correlation potential in the $X\alpha$ method can be considered as arising from a Fermi hole of uniform density.[1–3] Gopinathan *et al.*[3] (GWB) derived an *ab initio* local-density exchange-correlation potential by considering a linear variation of the Fermi-hole density with appropriate boundary conditions. This potential could also be discussed in terms of the α parameter of the $X\alpha$ method. Later it was suggested[4] that the self-interaction part of the exchange-correlation potential could be evaluated exactly and only the remaining "pure exchange" part need be approximated. In the original version,[4] the pure exchange part was approximated as in the $X\alpha$ method, leading to the exchange potential

$$U_{\uparrow}^{\mathrm{ex}}(r)=-9C\alpha_{\uparrow}\left[\sum_{i\uparrow}\rho_{i'\uparrow}(r)\rho_{\uparrow}^{-2/3}(r)n_i u_{i\uparrow}^{*}(r)u_{i\uparrow}(r)\right]\Big/\rho_{\uparrow}(r) \tag{1}$$

with $C=(3/4\pi)^{1/3}$, $\alpha_{\uparrow}=\frac{8}{27}(4\pi^2/3)^{1/3}(1/n_{\uparrow}+\frac{1}{2})/(1/n_{\uparrow}+\frac{1}{3})^{2/3}$, and $\rho_{i'\uparrow}(r)=\sum_{j(\neq i)}n_j u_{j\uparrow}^{*}(r)u_{j\uparrow}(r)$; $u_{j\uparrow}$ is a spin orbital of up spin with occupancy n_j and $n_{\uparrow}$ is the total number of up-spin electrons.

Tseng and Whitehead[5] later recognized that the α used above was not applicable in Eq. (1) since this α was derived for the total exchange-correlation potential according to the GWB formalism and not for the pure exchange part given by Eq. (1). Hence these authors parametrized the potential of Eq. (1), adjusting α such that it reproduces the total Hartree-Fock energy of the atom as close as possible. They also named the method of Ref. 4 as the Ξ_a method, Ξ to denote the separation of the self-interaction part and subscript a to emphasize its distinction from α. Tseng and Whitehead[6] (TW) also formulated a theoretical model for the exchange hole and derived an expression for a. However, these theoretical values of a were consistently higher than the corresponding parameterized values as can be seen from Fig. 1. This discrepancy can be traced to a certain violation of charge conservation in their model.

The pure exchange charge removed from the exchange hole is given by

$$\int \rho^{\mathrm{ex}}(r)d\tau=\int \rho^{\mathrm{xc}}(r)d\tau-\int n_i u_i^{*}(r)u_i(r)d\tau\ . \tag{2}$$

The first term on the right-hand side is the total exchange-correlation charge removed from the Fermi hole, which is known to be[1] a unit electron charge in magnitude. The second term is the self-interaction charge which is also unity in magnitude since the spin orbital u_i is singly occupied and normalized. Therefore the total charge removed from the pure exchange hole is zero.

This charge requirement is violated in the TW model as can be seen from the schematic representation of the exchange charge distribution of the TW model (see Fig. 2). Moreover, the assumption that $\rho_i(r)=\rho(r)/n$, on which their derivation is based, is not valid at all r, though it may be good at large distances. The purpose of the present communication is to derive an *ab initio* exchange potential that satisfies the above charge requirement and to test it for a variety of atoms by calculating the one-electron eigenvalues and total energies.

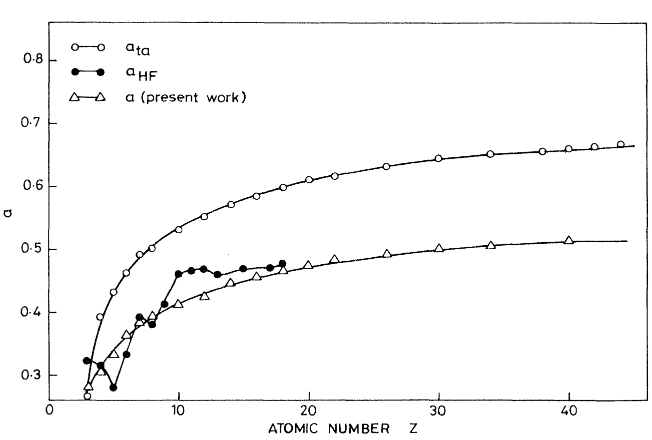

FIG. 1. Comparison of a [present work, Eq. (17)] with the theoretically derived a_{ta} (Ref. 6) and the parametrized values a_{HF} (Ref. 5).

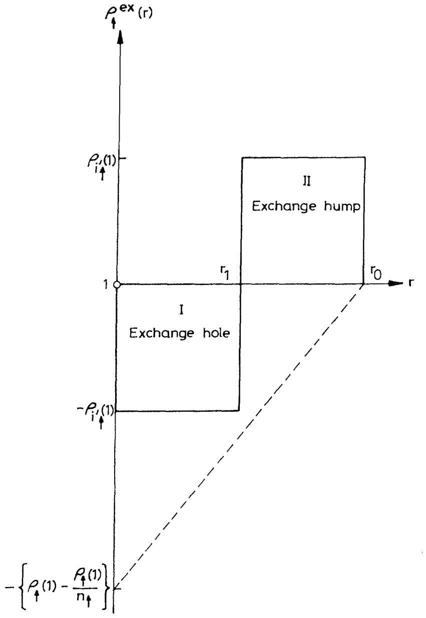

FIG. 2. Schematic representation of the variation of the exchange charge density with distance r, from the reference electron. — — —, model from Ref. 6; ——, present model.

II. EXCHANGE POTENTIAL IN THE Ξ METHOD

It is to be noted that the original formalism of Ref. 4 and its later modification in Ref. 6 as well as the present modification should be designated as the Ξ method, since there is no adjustable parameter involved in the potential. However, the parametric version of Ref. 5 may be designated as Ξ_a. We shall adopt this nomenclature hereafter.

The exchange hole density must be negative in the neighborhood of the reference electron (whose position is at the origin in Fig. 2) corresponding to the removal of electrons of the same spin from its vicinity due to Fermi correlation. This gives rise to a negative exchange potential. As noted above, the total charge removed from the exchange hole must be zero and hence the charge removed from the vicinity of the reference electron must reappear at farther distances. Hence the exchange density and consequently the exchange potential become positive in the region beyond a finite distance, say r_1 in Fig. 2, from the reference electron. We may call this region (labeled II in Fig. 2) as an *"exchange hump"* as opposed to the *"exchange hole"* of region I. However, the net exchange potential is negative since charge is removed at small distances from the reference electron and placed at larger distances.

It is known that[3] the Fermi hole density at the position of the reference electron (say at point 1) is $-\rho_\uparrow(1)$, where $\rho_\uparrow(1)$ is the total density of all the up-spin electrons at the site of the reference electron (hereafter we take reference electron i to be up in spin and occupying spin orbital u_i). In the Ξ method self-interaction is removed from the total exchange correlation. Hence the pure exchange density at the site of the reference electron is $-\rho_{i'\uparrow}(1)$ of Eq. (1). $\rho_{i'\uparrow}(1)$ is simply the density of all up-spin electrons minus that of the reference electron, at point 1.

To make the exchange potential analytically derivable, we presently make the following assumptions. (1) The exchange hole and hump are spherically symmetric. (2) The exchange density has the same constant magnitude $\rho_{i'\uparrow}(1)$ throughout the hole and hump. (3) The exchange density is zero beyond a finite distance, say, r_0 from the reference electron. (4) The radius (r_0) of the "exchange hole + hump" is taken to be the same as that of the Fermi hole (r_F). Assumptions 1 and 3 are the same as that made in the earlier treatments[1-6] of the exchange and the Fermi holes, while 2 is similar to the Slater's assumption for the Fermi hole[1,2] in the $X\alpha$ method. Assumption 4 can be rationalized as follows. It is reasonable to expect that the pure exchange charge density extends throughout the Fermi hole and hence $r_0=r_F$. Moreover, the ratio of the pure exchange energy to the total exchange-correlation energy, calculated in the present method, for the atoms Ne, Ar, Kr, and Xe are 0.17, 0.24, 0.36, and 0.42, respectively. It is evident from this that the contribution of the pure exchange potential to the total exchange-correlation potential is small and that the self-interaction potential is the dominant part. Hence it is valid to assume that the radius of the Fermi hole is not very much altered by the nature of the approximation used to treat the relatively small pure exchange potential. A similar assumption is implied in the treatment of the exchange hole by Tseng and Whitehead.[6] The exchange density distribution corresponding to these assumptions is shown in Fig. 2.

Since the charge removed from the exchange hole must be equal to that placed in the exchange hump, we have from the above assumptions

$$4\pi\rho_{i'\uparrow}(1)\int_0^{r_1} r^2dr=4\pi\rho_{i'\uparrow}(1)\int_{r_1}^{r_0} r^2dr\ . \tag{3}$$

Equation (3) leads directly to

$$r_1=2^{-1/3}r_0\ . \tag{4}$$

The potential produced at the site of the reference electron due to the exchange charge distribution of the "hole + hump" of Fig. 2 is

$$\begin{aligned}U_{i\uparrow}^{\rm ex}(1)&=-4\pi\rho_{i'\uparrow}(1)\int_0^{r_1} r\,dr+4\pi\rho_{i'\uparrow}(1)\int_{r_1}^{r_0} r\,dr\\&=-4\pi\rho_{i'\uparrow}(1)(2^{1/3}-1)r_0^2\end{aligned} \tag{5}$$

in Rydberg units. We have used Eq. (4) to obtain Eq. (5). It has been shown earlier in the GWB formalism[3] that the Fermi hole has a radius given by

$$r_F=[\pi\rho_\uparrow(1)(1/n_\uparrow+\tfrac{1}{3})]^{-1/3}\ . \tag{6}$$

Using assumption 4 and Eq. (6) in Eq. (5) we have,

$$\begin{aligned}U_{i\uparrow}^{\rm ex}(1)=&-4\pi^{1/3}(2^{1/3}-1)(1/n_\uparrow+\tfrac{1}{3})^{-2/3}\\&\times\rho_{i'\uparrow}(1)\rho_\uparrow^{-2/3}(1)\ .\end{aligned} \tag{7}$$

Equation (7) represents the exchange potential of the present Ξ method. To complete the specification of the Ξ method we recall the relevant equations from Ref. 4. The total energy of the atom can be written as

TABLE I. Theoretical exchange parameter a for atoms defined by Eqs. (16) and (17) of the text.

Atom	Configuration	a	a_{HF}[a]
$_{3}$Li	He $2s^{1}$	0.280 367	0.322 37
$_{4}$Be	He $2s^{2}$	0.307 982	0.313 66
$_{5}$B	He $2s^{2}2p^{1}$	0.337 622	0.280 67
$_{6}$C	He $2s^{2}2p^{2}$	0.363 097	0.331 27
$_{7}$N	He $2s^{2}2p^{3}$	0.384 213	0.390 28
$_{8}$O	He $2s^{2}2p^{4}$	0.393 209	0.381 87
$_{9}$F	He $2s^{2}2p^{5}$	0.404 016	0.416 79
$_{10}$Ne	He $2s^{2}2p^{6}$	0.414 705	0.462 33
$_{11}$Na	Ne $3s^{1}$	0.424 650	0.466 48
$_{12}$Mg	Ne $3s^{2}$	0.432 937	0.466 32
$_{13}$Al	Ne $3s^{2}3p^{1}$	0.440 644	0.462 22
$_{14}$Si	Ne $3s^{2}3p^{2}$	0.447 712	0.463 66
$_{15}$P	Ne $3s^{2}3p^{3}$	0.454 156	0.468 36
$_{16}$S	Ne $3s^{2}3p^{4}$	0.459 093	0.466 27
$_{17}$Cl	Ne $3s^{2}3p^{5}$	0.463 828	0.471 17
$_{18}$Ar	Ne $3s^{2}3p^{6}$	0.468 303	0.479 16
$_{19}$K	Ar $4s^{1}$	0.472 498	
$_{20}$Ca	Ar $4s^{2}$	0.476 274	
$_{21}$Sc	Ar $3d^{1}4s^{2}$	0.479 825	
$_{22}$Ti	Ar $3d^{2}4s^{2}$	0.483 156	
$_{23}$V	Ar $3d^{3}4s^{2}$	0.486 276	
$_{24}$Cr	Ar $3d^{5}4s^{1}$	0.489 600	
	Ar $3d^{4}4s^{2}$	0.489 199	
$_{25}$Mn	Ar $3d^{5}4s^{2}$	0.491 937	
$_{26}$Fe	Ar $3d^{6}4s^{2}$	0.494 203	
$_{27}$Co	Ar $3d^{7}4s^{2}$	0.496 385	
$_{28}$Ni	Ar $3d^{8}4s^{2}$	0.498 475	
$_{29}$Cu	Ar $3d^{10}4s^{1}$	0.500 473	
$_{30}$Zn	Ar $3d^{10}4s^{2}$	0.502 379	
$_{31}$Ga	Ar $3d^{10}4s^{2}4p^{1}$	0.504 195	
$_{32}$Ge	Ar $3d^{10}4s^{2}4p^{2}$	0.505 925	
$_{33}$As	Ar $3d^{10}4s^{2}4p^{3}$	0.507 574	
$_{34}$Se	Ar $3d^{10}4s^{2}4p^{4}$	0.509 077	
$_{35}$Br	Ar $3d^{10}4s^{2}4p^{5}$	0.510 519	
$_{36}$Kr	Ar $3d^{10}4s^{2}4p^{6}$	0.511 903	
$_{37}$Rb	Kr $5s^{1}$	0.513 229	
$_{38}$Sr	Kr $5s^{2}$	0.514 486	
$_{39}$Y	Kr $4d^{1}5s^{2}$	0.515 691	
$_{40}$Zr	Kr $4d^{2}5s^{2}$	0.516 850	
$_{41}$Nb	Kr $4d^{4}5s^{1}$	0.518 007	
$_{42}$Mo	Kr $4d^{5}5s^{1}$	0.519 082	
$_{43}$Tc	Kr $4d^{5}5s^{2}$	0.520 056	
$_{44}$Ru	Kr $4d^{7}5s^{1}$	0.520 998	
$_{45}$Rh	Kr $4d^{8}5s^{1}$	0.521 910	
$_{46}$Pd	Kr $4d^{10}$	0.522 784	
$_{47}$Ag	Kr $4d^{10}5s^{1}$	0.523 643	
$_{48}$Cd	Kr $4d^{10}5s^{2}$	0.524 466	
$_{49}$In	Kr $4d^{10}5s^{2}5p^{1}$	0.525 262	
$_{50}$Sn	Kr $4d^{10}5s^{2}5p^{2}$	0.526 031	
$_{51}$Sb	Kr $4d^{10}5s^{2}5p^{3}$	0.526 775	
$_{52}$Te	Kr $4d^{10}5s^{2}5p^{4}$	0.527 481	
$_{53}$I	Kr $4d^{10}5s^{2}5p^{5}$	0.528 165	
$_{54}$Xe	Kr $4d^{10}5s^{2}5p^{6}$	0.528 828	
$_{55}$Cs	Xe $6s^{1}$	0.529 471	
$_{56}$Ba	Xe $6s^{2}$	0.530 090	
$_{57}$La	Xe $5d^{1}6s^{2}$	0.530 692	
$_{58}$Ce	Xe $4f^{2}6s^{2}$	0.531 276	
$_{59}$Pr	Xe $4f^{3}6s^{2}$	0.531 843	
$_{60}$Nd	Xe $4f^{4}6s^{2}$	0.532 394	
$_{61}$Pm	Xe $4f^{5}6s^{2}$	0.532 928	
$_{62}$Sm	Xe $4f^{6}6s^{2}$	0.533 448	
$_{63}$Eu	Xe $4f^{7}6s^{2}$	0.533 953	
$_{64}$Gd	Xe $4f^{7}5d^{1}6s^{2}$	0.534 443	
$_{65}$Tb	Xe $4f^{8}5d^{1}6s^{2}$	0.534 904	
$_{66}$Dy	Xe $4f^{10}6s^{2}$	0.535 344	
$_{67}$Ho	Xe $4f^{11}6s^{2}$	0.535 785	
$_{68}$Er	Xe $4f^{12}6s^{2}$	0.536 214	
$_{69}$Tm	Xe $4f^{13}6s^{2}$	0.536 634	
$_{70}$Yb	Xe $4f^{14}6s^{2}$	0.537 042	
$_{71}$Lu	Xe $4f^{14}5d^{1}6s^{2}$	0.537 441	
$_{72}$Hf	Xe $4f^{14}5d^{2}6s^{2}$	0.537 830	
$_{73}$Ta	Xe $4f^{14}5d^{3}6s^{2}$	0.538 209	
$_{74}$W	Xe $4f^{14}5d^{4}6s^{2}$	0.538 580	
$_{75}$Re	Xe $4f^{14}5d^{5}6s^{2}$	0.538 942	
$_{76}$Os	Xe $4f^{14}5d^{6}6s^{2}$	0.539 290	
$_{77}$Ir	Xe $4f^{14}5d^{7}6s^{2}$	0.539 630	
$_{78}$Pt	Xe $4f^{14}5d^{9}6s^{1}$	0.539 962	
$_{79}$Au	Xe $4f^{14}5d^{10}6s^{1}$	0.540 287	
$_{80}$Hg	Xe $4f^{14}5d^{10}6s^{2}$	0.540 605	
$_{81}$Tl	Xe $4f^{14}5d^{10}6s^{2}6p^{1}$	0.540 916	
$_{82}$Pb	Xe $4f^{14}5d^{10}6s^{2}6p^{2}$	0.541 220	
$_{83}$Bi	Xe $4f^{14}5d^{10}6s^{2}6p^{3}$	0.541 517	
$_{84}$Po	Xe $4f^{14}5d^{10}6s^{2}6p^{4}$	0.541 806	
$_{85}$At	Xe $4f^{14}5d^{10}6s^{2}6p^{5}$	0.542 089	
$_{86}$Rn	Xe $4f^{14}5d^{10}6s^{2}6p^{6}$	0.542 366	
$_{87}$Fr	Rn $7s^{1}$	0.542 637	
$_{88}$Ra	Rn $7s^{2}$	0.542 903	
$_{89}$Ac	Rn $6d^{1}7s^{2}$	0.543 163	
$_{90}$Th	Rn $6d^{2}7s^{2}$	0.543 417	
$_{91}$Pa	Rn $5f^{2}6d^{1}7s^{2}$	0.543 667	
$_{92}$U	Rn $5f^{3}6d^{1}7s^{2}$	0.543 912	
$_{93}$Np	Rn $5f^{5}7s^{2}$	0.544 152	
$_{94}$Pu	Rn $5f^{6}7s^{2}$	0.544 387	
$_{95}$Am	Rn $5f^{7}7s^{2}$	0.544 618	
$_{96}$Cm	Rn $5f^{7}6d^{1}7s^{2}$	0.544 844	
$_{97}$Bk	Rn $5f^{8}6d^{1}7s^{2}$	0.545 063	
$_{98}$Cf	Rn $5f^{10}7s^{2}$	0.545 275	
$_{99}$Es	Rn $5f^{11}7s^{2}$	0.545 486	
$_{100}$Fm	Rn $5f^{12}7s^{2}$	0.545 693	
$_{101}$Md	Rn $5f^{13}7s^{2}$	0.545 897	
$_{102}$No	Rn $5f^{14}7s^{2}$	0.546 097	
$_{103}$Lw	Rn $5f^{14}6d^{1}7s^{2}$	0.546 294	

[a] Parametrized values of a from Ref. 5. No values are given for $Z > 18$.

$$\langle E\rangle=\sum_i n_i\int u_i^*(r)f_1u_i(r)dr+\frac{1}{2}\int\rho(r)\rho(r')g_{rr'}dr\,dr'+\frac{1}{2}\int\rho_\uparrow(r)U_\uparrow^{\mathrm{xc}}(r)dr+\frac{1}{2}\int\rho_\downarrow(r)U_\downarrow^{\mathrm{xc}}(r)dr \qquad (8)$$

with $f_1=-\nabla^2-2Z/r$ and $g_{rr'}=2/|r-r'|$. The exchange-correlation potential is separated into a self-interaction part and a pure exchange part as

$$U_\uparrow^{\mathrm{xc}}(r)=U_\uparrow^{s}(r)+U_\uparrow^{\mathrm{ex}}(r)\ . \qquad (9)$$

TABLE II. Comparison of orbital energies ($-\epsilon_i$) for various atoms and ions calculated using $V^{\text{ex}}(\Xi_{\text{present}})$, $V^{\text{ex}}(\Xi_{\text{TW}})$ of Ref. 6, and $V^{\text{ex}}(\Xi_G)$ of Ref. 4 with exact HF energies. Energies are in rydbergs. Note that these energies are obtained using Ξ_{present}, Ξ_{TW}, and Ξ_G wave functions in the HF expression for eigenvalue (Ref. 8).

Atom[a]	Orbital	$-\epsilon_i^{\text{HF}^{\text{b}}}$	$-\epsilon_i^{\text{HF}}(\Xi_{\text{present}})$	$-\epsilon_i^{\text{HF}}(\Xi_{\text{TW}})$	$-\epsilon_i^{\text{HF}}(\Xi_G)$
Ne$1s^22s^22p^6\ {}^1S$	1s	65.5449	65.2374	64.8962	64.2793
	2s	3.8608	3.7679	3.6438	3.4110
	2p	1.7008	1.6225	1.4959	1.2496
Ar	1s	237.2207	236.6410	236.0572	235.4851
[Ne]$3s^23p^6\ {}^1S$	2s	24.6443	24.4052	24.0795	23.7466
	2p	19.1429	18.8963	18.5467	18.1823
	3s	2.5547	2.5172	2.4106	2.3008
	3p	1.1820	1.1526	1.0574	0.9543
Kr	1s	1040.3309	1039.1764	1037.8902	1037.3005
[Ar]$3d^{10}4s^24p^6\ {}^1S$	2s	139.8062	139.1398	138.2094	137.7340
	2p	126.0196	125.3028	124.3286	123.8290
	3s	21.6989	21.4613	20.9958	20.7556
	3p	16.6630	16.4274	15.9579	15.7159
	3d	7.6505	7.4145	6.9306	6.6821
	4s	2.3059	2.2680	2.1443	2.0810
	4p	1.0484	1.0179	0.9161	0.8617
Xe	1s	2448.7956	2447.1782	2445.4560	2444.8671
[Kr]$4d^{10}5s^25p^6\ {}^1S$	2s	378.6802	377.7352	376.3990	375.9651
	2p	355.5649	354.5505	353.1500	352.6934
	3s	80.3513	79.9198	79.1080	78.8340
	3p	70.4433	70.0012	69.1624	68.8804
	3d	52.2378	51.7599	50.8685	50.5668
	4s	15.7126	15.5531	15.1415	15.0033
	4p	12.0167	11.8624	11.4606	11.3270
	4d	5.5558	5.4148	5.0436	4.9179
	5s	1.8888	1.8501	1.7337	1.6941
	5p	0.9146	0.8817	0.7865	0.7529
Sc	1s↑	331.7998	331.1061	330.4349	329.9130
[Ar]$3d^14s^2\ {}^2D$	1s↓		331.1068	330.4360	329.9122
	2s↑	38.1612	37.8373	37.4360	37.0919
	2s↓		37.8372	37.4361	37.0928
	2p↑	31.3365	30.9981	30.5664	30.1966
	2p↓		30.9982	30.5667	30.1973
	3s↑	5.1346	5.0399	4.8741	4.7326
	3s↓		5.0394	4.8730	4.7319
	3p↑	3.1491	3.0592	2.8995	2.7614
	3p↓		3.0585	2.8985	2.7604
	3d↑	0.6874	0.6221	0.5201	0.4183
	4s↑	0.4202	0.4126	0.3819	0.3526
	4s↓		0.4044	0.3793	0.3554
Ti	1s↑	366.5455	365.8331	365.1047	364.5628
[Ar]$3d^24s^2\ {}^3F$	1s↓		365.8343	365.1066	364.5614
	2s↑	42.8458	42.5024	42.0482	41.6820
	2s↓		42.5027	42.0488	41.6839
	2p↑	35.5824	35.2267	34.7367	34.3451
	2p↓		35.2271	34.7375	34.3465
	3s↑	5.7468	5.6486	5.4522	5.2956
	3s↓		5.6460	5.4495	5.2936
	3p↑	3.5902	3.4957	3.3068	3.1536
	3p↓		3.4932	3.3048	3.1520
	3d↑	0.8813	0.7297	0.5949	0.4746
	4s↑	0.4416	0.4357	0.3993	0.3663
	4s↓		0.4228	0.3962	0.3724

TABLE II. (*Continued.*)

Atom[a]	Orbital	$-\epsilon_i^{\mathrm{HF}^b}$	$-\epsilon_i^{\mathrm{HF}}(\Xi_{\mathrm{present}})$	$-\epsilon_i^{\mathrm{HF}}(\Xi_{\mathrm{TW}})$	$-\epsilon_i^{\mathrm{HF}}(\Xi_G)$
V	$1s\uparrow$	403.0057	401.2541	401.4763	400.9313
$[\mathrm{Ar}]3d^3 4s^2\ {}^4F$	$1s\downarrow$		402.2559	401.4791	400.9290
	$2s\uparrow$	47.7493	47.3794	46.8722	46.4892
	$2s\downarrow$		47.3805	46.8734	46.4894
	$2p\uparrow$	40.0450	39.6566	39.1166	38.7067
	$2p\downarrow$		39.6577	39.1181	38.7089
	$3s\uparrow$	6.3664	6.2589	6.0336	5.8664
	$3s\downarrow$		6.2551	6.0293	5.8636
	$3p\uparrow$	4.0385	3.9345	3.7175	3.5539
	$3p\downarrow$		3.9306	3.7144	3.5518
	$3d\uparrow$	1.0192	0.8215	0.6559	0.5218
	$4s\uparrow$	0.4612	0.4562	0.4147	0.3795
	$4s\downarrow$		0.4390	0.4116	0.3886
Cr	$1s\uparrow$	441.1845	440.3861	439.5720	438.9705
$[\mathrm{Ar}]3d^4 4s^2\ {}^5D$	$1s\downarrow$		440.3885	439.5761	438.9700
	$2s\uparrow$	52.8783	52.4769	51.9200	51.5180
	$2s\downarrow$		52.4797	51.9205	51.5217
	$2p\uparrow$	44.7306	44.3094	43.7199	43.2901
	$2p\downarrow$		44.3113	43.7187	43.2931
	$3s\uparrow$	6.9982	6.8795	6.6246	6.4487
	$3s\downarrow$		6.8729	6.6194	6.4458
	$3p\uparrow$	4.4977	4.3829	4.1367	3.9645
	$3p\downarrow$		4.3761	4.1325	3.9627
	$3d\uparrow$	1.1383	0.9039	0.7078	0.5624
	$4s\uparrow$	0.4795	0.4749	0.4294	0.3929
	$4s\downarrow$		0.4542	0.4257	0.4040
Mn	$1s\uparrow$	481.0680	480.2352	479.3681	478.8008
$[\mathrm{Ar}]3d^5 4s^2\ {}^6S$	$1s\downarrow$		480.2381	479.3761	478.7971
	$2s\uparrow$	58.2190	57.8023	57.1871	56.7732
	$2s\downarrow$		57.8050	57.1899	56.7781
	$2p\uparrow$	49.6252	49.1878	48.5355	48.0966
	$2p\downarrow$		49.1902	48.5385	48.0999
	$3s\uparrow$	7.6333	7.5141	7.2302	7.0436
	$3s\downarrow$		7.5066	7.2234	7.0401
	$3p\uparrow$	4.9591	4.8438	4.5684	4.3855
	$3p\downarrow$		4.8346	4.5630	4.3833
	$3d\uparrow$	1.2777	0.9799	0.7530	0.5945
	$4s\uparrow$	0.4957	0.4926	0.4430	0.4050
	$4s\downarrow$		0.4689	0.4397	0.4182
Fe[c]	$1s\uparrow$	522.7489	521.8842	520.9488	520.3398
$[\mathrm{Ar}]3d^6 4s^2\ {}^5D$	$1s\downarrow$	522.7497	521.8864	520.9522	520.3392
	$2s\uparrow$	63.9986	63.4209	62.7630	62.3295
	$2s\downarrow$	63.7529	63.4172	62.7685	62.3322
	$2p\uparrow$	54.9506	54.3506	53.6579	53.1974
	$2p\downarrow$	54.7133	54.3530	53.6633	53.1981
	$3s\uparrow$	8.6972	8.2036	7.8974	7.6956
	$3s\downarrow$	7.9881	8.1952	7.8922	7.6928
	$3p\uparrow$	5.9166	5.3511	5.0543	4.8555
	$3p\downarrow$	5.0591	5.3430	5.0502	4.8567
	$3d\uparrow$	1.3761	1.0798	0.8306	0.6563
	$3d\downarrow$	0.9374	1.0305	0.7978	0.6418
	$4s\uparrow$	0.4554	0.5069	0.4566	0.4190
	$4s\downarrow$	0.4844	0.4927	0.4578	0.4314

TABLE II. (*Continued.*)

Atom[a]	Orbital	$-\epsilon_i^{\mathrm{HF}^{\mathrm{b}}}$	$-\epsilon_i^{\mathrm{HF}}(\Xi_{\mathrm{present}})$	$-\epsilon_i^{\mathrm{HF}}(\Xi_{\mathrm{TW}})$	$-\epsilon_i^{\mathrm{HF}}(\Xi_G)$
Co	1s↑	566.1310	565.2142	564.2551	563.6682
[Ar]$3d^7 4s^2$ ^4F	1s↓		565.2159	564.2576	563.6649
	2s↑	69.7367	69.2625	68.5652	68.1073
	2s↓		69.2648	68.5618	68.1084
	2p↑	60.2403	59.7408	59.0014	58.5186
	2p↓		59.7370	59.0060	58.5209
	3s↑	9.0486	8.9038	8.5743	8.3607
	3s↓		8.8973	8.5709	8.3582
	3p↑	6.0125	5.8690	5.5495	5.3394
	3p↓		5.8627	5.5463	5.3384
	3d↑	1.3508	1.1710	0.8986	0.7116
	3d↓		1.1357	0.8761	0.7021
	4s↑	0.5348	0.5216	0.4708	0.4339
	4s↓		0.5127	0.4729	0.4434
Ni	1s↑	611.2381	610.2800	609.2860	608.6620
[Ar]$3d^8 4s^2$ ^3F	1s↓		610.2810	609.2873	608.6597
	2s↑	75.8357	75.3325	74.5905	74.1120
	2s↓		75.3362	74.5925	74.1135
	2p↑	65.8835	65.3500	64.5692	64.0649
	2p↓		65.3517	64.5710	64.0648
	3s↑	9.7757	9.6186	9.2680	9.0395
	3s↓		9.6146	9.2659	9.0381
	3p↑	6.5554	6.4003	6.0578	5.8344
	3p↓		6.3955	6.0556	5.8335
	3d↑	1.4139	1.2559	0.9609	0.7604
	3d↓		1.2330	0.9471	0.7548
	4s↑	0.5525	0.5364	0.4852	0.4485
	4s↓		0.5311	0.4868	0.4549
Cu[d]	1s↑	657.5867	656.5664	655.4824	654.8142
[Ar]$3d^{10} 4s^1$ ^2S	1s↓		656.5670	655.4834	654.8145
	2s↑	81.6398	81.1042	80.2543	79.7197
	2s↓		81.1107	80.2493	79.7174
	2p↑	71.2377	70.6744	69.7796	69.2217
	2p↓		70.6735	69.7768	69.2177
	3s↑	10.0264	9.8637	9.4381	9.1772
	3s↓		9.8641	9.4387	9.1779
	3p↑	6.6523	6.4937	6.0821	5.8289
	3p↓		6.4944	6.0829	5.8295
	3d↑	0.9856	0.8413	0.5061	0.2917
	3d↓		0.8648	0.5201	0.2991
	4s↑	0.4735	0.4714	0.4255	0.3944
Zn	1s	706.6091	705.6072	704.4182	703.8173
[Ar]$3d^{10} 4s^2$ ^1S	2s	88.7235	88.1732	87.3305	86.8211
	2p	77.8497	77.2670	76.3801	75.8465
	3s	11.2756	11.1012	10.6975	10.4565
	3p	7.6788	7.5049	7.1104	6.8741
	3d	1.5651	1.4110	1.0653	0.8528
	4s	0.5850	0.5647	0.5125	0.4780
Ga	1s↑	757.6369	756.6057	755.4637	754.7524
[Zn]$4p^1$ ^2P	1s↓		756.6061	755.4643	754.7523
	2s↑	96.3368	95.7593	94.9106	94.4124
	2s↓		95.7589	94.9103	94.4114
	2p↑	84.9881	84.3738	83.4819	82.9596

TABLE II. *(Continued.)*

Atom[a]	Orbital	$-\epsilon_i^{\mathrm{HF}}$[b]	$-\epsilon_i^{\mathrm{HF}}(\Xi_{\mathrm{present}})$	$-\epsilon_i^{\mathrm{HF}}(\Xi_{\mathrm{TW}})$	$-\epsilon_i^{\mathrm{HF}}(\Xi_G)$
	$2p\downarrow$		84.3736	83.4819	82.9590
	$3s\uparrow$	12.7893	12.5991	12.1953	11.9599
	$3s\downarrow$		12.5987	12.1952	11.9608
	$3p\uparrow$	8.9647	8.7757	8.3782	8.1455
	$3p\downarrow$		8.7754	8.3782	8.1456
	$3d\uparrow$	2.3867	2.2142	1.8477	1.6291
	$3d\downarrow$		2.2146	1.8483	1.6298
	$4s\uparrow$	0.8492	0.8185	0.7572	0.7198
	$4s\downarrow$		0.8243	0.7553	0.7122
	$4p\uparrow$	0.4170	0.4015	0.3654	0.3400
Ge	$1s\uparrow$	810.4889	809.4151	808.2558	807.5858
[Zn]$4p^2$ ^3P	$1s\downarrow$		809.4159	808.2572	807.5857
	$2s\uparrow$	104.3007	103.7043	102.8402	102.3537
	$2s\downarrow$		103.7035	102.8396	102.3518
	$2p\uparrow$	92.4723	91.8378	90.9288	90.4183
	$2p\downarrow$		91.8373	90.9287	90.4169
	$3s\uparrow$	14.3820	14.1814	13.7652	13.5387
	$3s\downarrow$		14.1808	13.7663	13.5381
	$3p\uparrow$	10.3232	10.1249	9.7125	9.4861
	$3p\downarrow$		10.1246	9.7125	9.4854
	$3d\uparrow$	3.2698	3.0842	2.6900	2.4699
	$3d\downarrow$		3.0854	2.6913	2.4713
	$4s\uparrow$	1.1067	1.0766	1.0008	0.9593
	$4s\downarrow$		1.0794	0.9949	0.9467
	$4p\uparrow$	0.5747	0.5144	0.4630	0.4323
As	$1s\uparrow$	865.1724	864.0938	862.8857	862.2275
[Zn]$4p^3$ ^4S	$1s\downarrow$		864.0949	862.8906	862.2273
	$2s\uparrow$	112.6196	112.0113	111.1232	110.6414
	$2s\downarrow$		112.0103	111.1225	110.6496
	$2p\uparrow$	100.3075	99.6576	98.7246	98.2196
	$2p\downarrow$		99.6570	98.7247	98.2169
	$3s\uparrow$	16.0592	15.8539	15.4260	15.1962
	$3s\downarrow$		15.8532	15.4258	15.1971
	$3p\uparrow$	11.7614	11.5571	11.1306	10.9011
	$3p\downarrow$		11.5563	11.1308	10.9018
	$3d\uparrow$	4.2253	4.0301	3.6124	3.3845
	$3d\downarrow$		4.0318	3.6143	3.3861
	$4s\uparrow$	1.3718	1.3439	1.2546	1.2077
	$4s\downarrow$		1.3437	1.2546	1.1918
	$4p\uparrow$	0.7390	0.6266	0.5600	0.5230
Se	$1s\uparrow$	921.7348	920.6283	919.3961	918.7196
[Zn]$4p^4$ ^3P	$1s\downarrow$		920.6290	919.6903	918.7195
	$2s\uparrow$	121.3378	120.7042	119.8020	119.3243
	$2s\downarrow$		120.7035	119.8016	119.3227
	$2p\uparrow$	108.5378	107.8635	106.9133	106.4123
	$2p\downarrow$		107.8632	106.9134	106.4111
	$3s\uparrow$	17.8642	17.6431	17.2082	16.9738
	$3s\downarrow$		17.6427	17.2081	16.9759
	$3p\uparrow$	13.3230	13.1039	12.6684	12.4347
	$3p\downarrow$		13.1038	12.6686	12.4351
	$3d\uparrow$	5.2992	5.0863	4.6497	4.4138
	$3d\downarrow$		5.0874	4.6508	4.4147

TABLE II. *(Continued.)*

Atom[a]	Orbital	$-\epsilon_i^{\mathrm{HF}^{\mathrm{b}}}$	$-\epsilon_i^{\mathrm{HF}}(\Xi_{\mathrm{present}})$	$-\epsilon_i^{\mathrm{HF}}(\Xi_{\mathrm{TW}})$	$-\epsilon_i^{\mathrm{HF}}(\Xi_G)$
	$4s\uparrow$	1.6748	1.6425	1.5425	1.4892
	$4s\downarrow$		1.6392	1.5375	1.4828
	$4p\uparrow$	0.8057	0.7570	0.6790	0.6352
	$4p\downarrow$		0.7496	0.6730	0.6293
Br	$1s\uparrow$	980.1207	978.9878	977.7269	977.0399
[Zn]$4p^5\ ^2P$	$1s\downarrow$		978.9882	977.7277	977.0400
	$2s\uparrow$	130.3999	129.7470	128.8357	128.3610
	$2s\downarrow$		129.7468	128.8355	128.3607
	$2p\uparrow$	117.1085	116.4135	115.4527	114.9534
	$2p\downarrow$		116.4133	115.4527	114.9532
	$3s\uparrow$	19.7438	19.5117	19.0606	18.8281
	$3s\downarrow$		19.5116	19.0606	18.8283
	$3p\uparrow$	14.9564	14.7264	14.2746	14.0385
	$3p\downarrow$		14.7264	14.2748	14.0387
	$3d\uparrow$	6.4404	6.2133	5.7532	5.5117
	$3d\downarrow$		6.2138	5.7537	5.5120
	$4s\uparrow$	1.9854	1.9489	1.8371	1.7788
	$4s\downarrow$		1.9473	1.8351	1.7764
	$4p\uparrow$	0.9142	0.8863	0.7964	0.7470
	$4p\downarrow$		0.8824	0.7939	0.7451
Na$^{+\,\mathrm{d}}$ $1s^22s^22p^6\ ^1S$	$1s$	81.5180	81.2118	80.8786	80.2769
	$2s$	6.1464	6.0539	5.9386	5.7183
	$2p$	3.5925	3.5131	3.3882	3.1447
K$^{+\,\mathrm{d}}$	$1s$	267.5065	266.9245	266.3391	265.7860
[Ne]$3s^23p^6\ ^1S$	$2s$	29.4169	29.1776	28.8601	28.5367
	$2p$	23.4773	23.2322	22.8845	22.5309
	$3s$	3.9265	3.8887	3.7873	3.6823
	$3p$	2.3401	2.3099	2.2147	2.1120
Mn$^{++\,\mathrm{e}}$	$1s\uparrow$	482.369	481.5891	480.8940	480.1671
[Ar]$3d^5\ ^6S$	$1s\downarrow$	482.374	481.5921	480.7079	480.1637
	$2s\uparrow$	59.663	59.1161	58.9548	58.1182
	$2s\downarrow$	59.633	59.1183	58.3759	58.1228
	$2p\uparrow$	51.044	50.5079	51.9067	49.4514
	$2p\downarrow$	50.781	50.5102	51.3963	49.4550
	$3s\uparrow$	9.323	8.8167	8.7995	8.3979
	$3s\downarrow$	8.494	8.8089	8.0934	8.3959
	$3p\uparrow$	6.753	6.1662	6.5659	5.7597
	$3p\downarrow$	5.745	6.1582	6.8812	5.7590
	$3d\uparrow$	2.576	2.3059	2.9375	1.9592
Cu$^{+\,\mathrm{f}}$	$1s$	658.22	657.2691	656.3205	655.4817
[Ar]$3d^{10}\ ^1S$	$2s$	82.26	81.7507	81.2308	80.3719
	$2p$	71.86	71.3240	72.6459	69.8774
	$3s$	10.65	10.5133	9.9071	9.8527
	$3p$	7.28	7.1555	6.9566	6.5174
	$3d$	1.62	1.5214	1.9398	0.9830
Rb$^{+\,\mathrm{g}}$	$1s$	1103.316	1102.1291	1100.8758	1100.2092
[Ar]$3d^{10}4s^24p^6\ ^1S$	$2s$	150.5	149.8393	148.9184	148.4517
	$2p$	136.214	135.5065	134.5365	134.0455
	$3s$	24.666	24.4327	23.9828	23.7539
	$3p$	19.376	19.1467	18.6887	18.4563

TABLE II. (*Continued.*)

Atom[a]	Orbital	$-\epsilon_i^{\mathrm{HF}^b}$	$-\epsilon_i^{\mathrm{HF}}(\Xi_{\mathrm{present}})$	$-\epsilon_i^{\mathrm{HF}}(\Xi_{\mathrm{TW}})$	$-\epsilon_i^{\mathrm{HF}}(\Xi_G)$
Rb$^+$	3*d*	9.866	9.6302	9.1570	8.9140
	4*s*	3.442	3.4053	3.2873	3.2264
	4*p*	2.018	1.9865	1.8842	1.8295

[a] Atom, configuration, and the ground-state multiplet.
[b] From C. F. Fischer, *The HF Method for Atoms* (Wiley, New York, 1977), for Ne through Br except for Fe and Cu atoms.
[c] P. S. Bagus and B. Liu, Phys. Rev. 148, 79 (1966).
[d] E. Clementi, IBM J. Res. Dev. Suppl. 9, 2 (1965).
[e] T. H. Wilson, J. H. Wood, and J. C. Slater, Phys. Rev. A 2, 620 (1970).
[f] J. B. Mann, Los Alamos Scientific Laboratory No. LA-3690 (unpublished).
[g] R. E. Watson and A. J. Freeman, Phys. Rev. 124, 1117 (1961).

The self-interaction part is evaluated exactly and is given by

$$U_\uparrow^s(r) = -\sum_{i\uparrow}\left[n_i u_i^*(r)u_i(r)\int n_i u_i^*(r')u_i(r')g_{rr'}dr'\right]\Big/\rho_\uparrow(r). \tag{10}$$

In the present Ξ method, $U_\uparrow^{\mathrm{ex}}(r)$ is given by the weighted average of $U_{i\uparrow}^{\mathrm{ex}}(r)$ [Eq. (7)] over all occupied up-spin orbitals:

$$U_\uparrow^{\mathrm{ex}} = -4\pi^{1/3}(2^{1/3}-1)(1/n_\uparrow+\tfrac{1}{3})^{-2/3} \times \sum_{i\uparrow}\rho_{i'\uparrow}(r)\rho_\uparrow^{-2/3}(r)n_i u_i^*(r)u_i(r)/\rho_\uparrow(r)\ . \tag{11}$$

Substitution of Eqs. (10) and (11) into Eq. (8) and application of the variational principle to $\langle E\rangle$ leads to the set of one-electron Schrödinger equations:

$$[f_1 + V^C(r) + V_i^s(r) + V_i^{\mathrm{ex}}(r)]u_{i\uparrow}(r) = \epsilon_i u_{i\uparrow}(r)\ , \tag{12}$$

where $V^C(r)$ is the Coulomb potential

$$V^C(r) = \sum_j n_j \int u_j^*(r')u_j(r')g_{rr'}dr' \tag{13}$$

and $V_{i\uparrow}^s(r)$ is the self-interaction potential of the electron in u_i,

$$V_{i\uparrow}^s(r) = -n_i\int u_{i\uparrow}^*(r')u_{i\uparrow}(r')g_{rr'}dr'\ . \tag{14}$$

$V_{i\uparrow}^{\mathrm{ex}}(r)$ is the variationally determined pure exchange po-

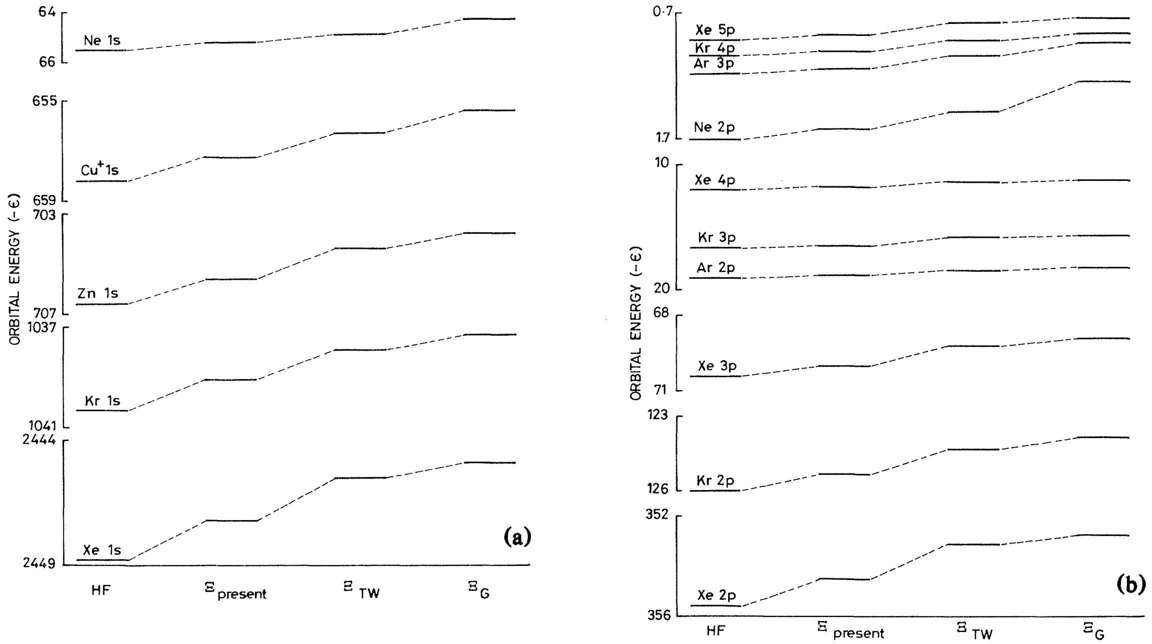

FIG. 3. (a) Comparison of the 1*s* orbital eigenvalues (rydbergs) calculated using $V^{\mathrm{ex}}(\Xi_{\mathrm{present}})$, $V^{\mathrm{ex}}(\Xi_{\mathrm{TW}})$ of Ref. 6, and $V^{\mathrm{ex}}(\Xi_G)$ of Ref. 4 with the exact HF energies. Energy values are obtained using the Ξ_{present}, Ξ_{TW}, and Ξ_G wave functions in the HF expression for energy eigenvalue of Ref. 8. Values are taken from Table II. (b) Comparison of *np* orbital eigenvalues calculated using various potentials. Symbols used here have the same meaning as in (a).

TABLE III. Total energies (in hartrees) of the ground-state multiplets for various atoms and ions obtained using Ξ_{present}, Ξ_{TW} of Ref. 6, and Ξ_G of Ref. 4 wave functions in the HF expression for total energy.

Atom	Configuration	Multiplet	$-E^{\text{HF}}$	$-E^{\text{HF}}(\Xi_{\text{present}})$[a]	$-E^{\text{HF}}(\Xi_{\text{TW}})$	$-E^{\text{HF}}(\Xi_G)$
Ne[b]	$1s^22s^22p^6$	^1S	128.5471	128.5279(1.92)	128.5007(4.64)	128.4126(13.45)
Ar	$[\text{Ne}]3s^23p^6$	^1S	526.8174	526.7993(1.81)	526.7384(7.90)	526.6620(15.54)
Kr	$[\text{Ar}]3d^{10}4s^24p^6$	^1S	2752.0546	2751.9575(9.71)	2751.8153(23.93)	2751.7422(31.24)
Xe	$[\text{Kr}]4d^{10}5s^25p^6$	^1S	7232.1302	7231.9045(22.57)	7231.6930(43.72)	7231.6210(50.92)
Sc	$[\text{Ar}]3d^14s^2$	^2D	759.7355	759.7008(3.47)	759.6208(11.47)	759.5864(14.91)
Ti	$[\text{Ar}]3d^24s^2$	^3F	848.4058	848.3812(2.46)	848.2824(12.34)	848.2476(15.82)
		^3P	848.3482	848.3230(2.52)	848.2210(12.72)	848.1825(16.57)
		^1G	848.3320	848.3063(2.57)	848.2031(12.89)	848.1638(16.82)
		^1D	848.3582	848.3334(2.48)	848.2317(12.65)	848.1935(16.47)
		^1S	848.2306	848.1965(3.41)	848.0867(14.39)	848.0430(18.76)
V	$[\text{Ar}]3d^34s^2$	^4F	942.8842	942.8528(3.14)	942.7524(13.18)	942.7124(17.18)
		^4P	942.8201	942.7884(3.17)	942.6847(13.54)	942.6427(17.74)
		^2H	942.7988	942.7668(3.20)	942.6619(13.69)	942.6191(17.97)
		^2G	942.8199	942.7883(3.16)	942.6844(13.55)	942.6423(17.76)
		^2F	942.7363	942.7025(3.38)	942.5942(14.21)	942.5495(18.68)
Cr	$[\text{Ar}]3d^44s^2$	^5D	1043.3095	1043.2659(4.36)	1043.1952(11.43)	1043.0875(22.20)
		^3H	1043.2223	1043.1782(4.41)	1043.1033(11.90)	1042.9932(22.91)
		^3G	1043.1993	1043.1548(4.45)	1043.0787(12.06)	1042.9681(23.12)
		^3D	1043.1672	1043.1220(4.52)	1043.0444(12.28)	1042.9329(23.43)
		^1I	1043.1793	1043.1344(4.49)	1043.0573(12.20)	1042.9460(23.33)
Mn	$[\text{Ar}]3d^54s^2$	^6S	1149.8657	1149.8082(5.75)	1149.7243(14.14)	1149.6840(18.17)
		^4G	1149.7228	1149.6648(5.80)	1149.5745(14.83)	1149.5308(19.20)
		^4F	1149.6268	1149.5671(5.97)	1149.4724(15.44)	1149.4266(20.02)
		^2I	1149.6629	1149.6041(5.88)	1149.5100(15.29)	1149.4658(19.71)
		^2H	1149.6167	1149.5569(5.98)	1149.4615(15.52)	1149.4153(20.14)
Fe	$[\text{Ar}]3d^64s^2$	^5D	1262.4432	1262.3893(5.39)	1262.2756(16.76)	1262.2087(23.45)
		^3H	1262.3437	1262.2900(5.37)	1262.1724(17.13)	1262.1032(24.05)
		^3G	1262.3173	1262.2635(5.38)	1262.1448(17.25)	1262.0750(24.23)
		^3D	1262.2805	1262.2263(5.42)	1262.1063(17.42)	1262.0356(24.49)
		^1I	1262.2944	1262.2404(5.40)	1262.1208(17.36)	1262.0503(24.41)
Co	$[\text{Ar}]3d^74s^2$	^4F	1381.4142	1381.3334(8.08)	1381.2435(17.07)	1381.2095(20.47)
		^4P	1381.3300	1381.2493(8.07)	1381.1566(17.34)	1381.1209(20.91)
		^2H	1381.3019	1381.2212(8.07)	1381.1274(17.45)	1381.0909(21.10)
		^2G	1381.3298	1381.2492(8.06)	1381.1563(17.35)	1381.1205(20.93)
		^2F	1381.2182	1381.1371(8.11)	1381.0405(17.77)	1381.0023(21.59)
Ni	$[\text{Ar}]3d^84s^2$	^3F	1506.8705	1506.7821(8.84)	1506.6901(18.04)	1506.6418(22.87)
		^3P	1506.7817	1506.6934(8.83)	1506.5988(18.29)	1506.5486(23.31)
		^1G	1506.7560	1506.6678(8.82)	1506.5722(18.38)	1506.5215(23.45)
		^1D	1506.7973	1506.7091(8.82)	1506.6149(18.24)	1506.5649(23.24)
		^1S	1506.5894	1506.5003(8.91)	1506.3992(19.02)	1506.3449(24.45)
Cu	$[\text{Ar}]3d^{10}4s^1$	^2S	1638.9628	1638.8426(12.02)	1638.7934(16.94)	1638.7205(24.23)
Zn	$[\text{Ar}]3d^{10}4s^2$	^1S	1777.8477	1777.7746(7.31)	1777.5908(25.69)	1777.5549(29.28)
Ga	$[\text{Ar}]3d^{10}4s^24p^1$	^2P	1923.2604	1923.1684(9.20)	1923.0534(20.70)	1922.9031(35.73)
Ge	$[\text{Ar}]3d^{10}4s^24p^2$	^3P	2075.3591	2075.2582(10.09)	2075.1585(20.06)	2075.0184(34.07)
		^1D	2075.3208	2075.2188(10.20)	2075.1170(20.38)	2074.9762(34.46)
As	$[\text{Ar}]3d^{10}4s^24p^3$	^4S	2234.2382	2234.1675(7.07)	2234.0015(23.67)	2233.8825(35.57)
		^2D	2234.1718	2234.0994(7.24)	2233.9312(24.06)	2233.8109(36.09)
		^2P	2234.1283	2234.0546(7.37)	2233.8843(24.40)	2233.7631(36.52)
Se	$[\text{Ar}]3d^{10}4s^24p^4$	^3P	2399.8658	2399.7963(6.95)	2399.6111(25.47)	2399.4766(38.92)
		^1D	2399.8185	2399.7473(7.12)	2399.5601(25.84)	2399.4247(39.38)
		^1S	2399.7466	2399.6737(7.29)	2399.4837(26.29)	2399.3469(39.97)
Br	$[\text{Ar}]3d^{10}4s^24p^5$	^2P	2572.4408	2572.3666(7.42)	2572.2075(23.33)	2572.0503(39.05)
Na^+[c]	$1s^22s^22p^6$	^1S	161.6768	161.6569(1.98)	161.6302(4.65)	161.5446(13.22)
K^+[c]	$[\text{Ne}]3s^23p^6$	^1S	599.0171	599.0020(1.51)	598.9249(9.22)	598.8646(15.25)

TABLE III. (*Continued.*)

Atom	Configuration	Multiplet	$-E^{\mathrm{HF}}$	$-E^{\mathrm{HF}}(\Xi_{\mathrm{present}})^{\mathrm{a}}$	$-E^{\mathrm{HF}}(\Xi_{\mathrm{TW}})$	$-E^{\mathrm{HF}}(\Xi_G)$
$\mathrm{Cu}^{+\,\mathrm{d}}$	$[\mathrm{Ar}]3d^{10}$	^1S	1638.73	1638.6730(5.70)	1638.5307(19.93)	1638.4792(25.08)
$\mathrm{Rb}^{+\,\mathrm{e}}$	$[\mathrm{Ar}]3d^{10}4s^24p^6$	^1S	2938.22	2938.1086(11.14)	2937.9498(27.02)	2937.7988(42.12)

[a] Values given in parentheses give absolute deviations from HF energies (E^{HF}), multiplied by 100.
[b] Ne through Br quoted from E. Clementi and C. Roetti, At. Data Nucl. Data Tables 14, No. 3 (1974); 14, No. 4 (1974).
[c] E. Clementi, IBM J. Res. Dev. Suppl. 9, 2 (1965).
[d] J. C. Slater, Int. J. Quantum Chem. Symp. 3, 727 (1970).
[e] R. E. Watson and A. J. Freeman, Phys. Rev. 124, 1117 (1961).

tential of the Ξ method and is given by

$$V_{i\uparrow}^{\mathrm{ex}}(r) = -4\pi^{1/3}(2^{1/3}-1)(1/n_\uparrow+\tfrac{1}{3})^{-2/3} \times[2\rho_{i'\uparrow}(r)\rho_\uparrow^{-2/3}(r) - \tfrac{2}{3}\rho_\uparrow^{-5/3}(r)\sum_{i\uparrow} n_i u_i^*(r)u_i(r)\rho_{i'\uparrow}(r)] \,. \tag{15}$$

The Ξ wave functions u_i and the eigenvalues ϵ_i are obtained as usual by the iterative solution of Eq. (12).

III. COMPARISON OF Ξ WITH PREVIOUS POTENTIALS

Even though the Ξ exchange potential does *not* depend on any adjustable parameter, it is convenient to derive the a values corresponding to the present potential for comparison with the theoretical as well as the parametric potentials of Tseng and Whitehead.[5,6] Comparing Eq. (11) with Eq. (1) and remembering that we now relabel α as a we have, for the present Ξ potential,

$$a_\uparrow = \pi^{2/3}(2^3-2^{8/3})3^{-7/3}(1/n_\uparrow+\tfrac{1}{3})^{-2/3} \,. \tag{16}$$

As in Ref. 3, we may use spin-averaged a values defined by

$$a = (n_\uparrow a_\uparrow + n_\downarrow a_\downarrow)/(n_\uparrow + n_\downarrow) \,. \tag{17}$$

The calculated values of a for all atoms are given in Table I together with the available parametric values of TW. Figure 1 shows that the present Ξ potential is very close to the parametrized TW potential unlike the theoretical TW potential. It is therefore clear that the present model of the exchange charge distribution of Fig. 2 is a substantial improvement over the theoretical TW potential and that the requirement of conservation of exchange charge is essential.

The a values corresponding to the Ξ potential increase with atomic number Z and reach a limiting value of 0.5673 as follows from Eq. (16) for large $n_\uparrow$. The same trend is observed for the a_{ta} values obtained using the theoretical Ξ_{TW} potential. The reason for the rather irregular variation of the parametrized values of Ref. 5 is not clear. Interestingly, Maessen and Schmidt[7] have reported that Gopinathan's exchange potential[4] gives dipole polarizability results for Cl^- in close agreement with Hartree-Fock values when $a=0.5$. This may be compared with the present theoretical value of 0.4683 for Cl^- calculated from Eq. (16).

In the case of hydrogen and helium atoms, where no exchange exists, the present Ξ exchange potential given by Eq. (15) goes to zero, as it should, since the density $\rho_{i'\uparrow}(r)$ defined by Eq. (11) is zero for these atoms. In other words, the a values defined by Eq. (16) are not applicable when $n_\uparrow$ is 1 or 0.

IV. ONE-ELECTRON AND TOTAL ENERGIES

Gopinathan and Rao[8] have pointed out that it is appropriate only to compare the energy values calculated by the Ξ wave function and the Hartree-Fock (HF) Hamiltonian, with the exact HF energy. This is because the total energy of the system calculated using the approximate wave function can only be compared with the exact

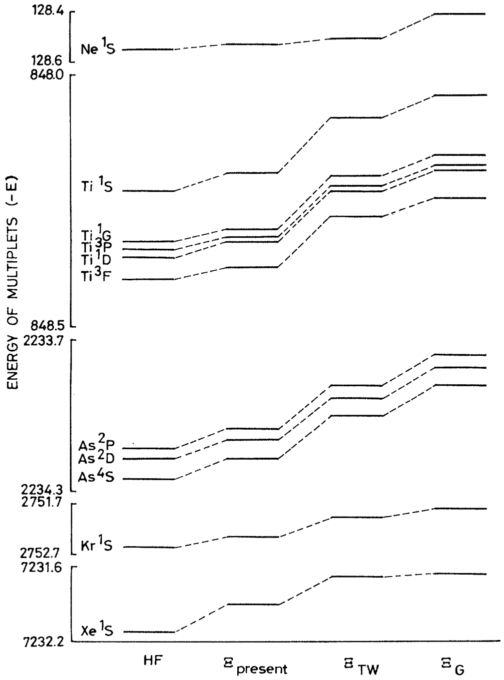

FIG. 4. Energy of the ground-state multiplets (in hartrees) obtained using the HF expression for energy and wave functions calculated with potentials Ξ_{present}, Ξ_{TW} of Ref. 6, and Ξ_G of Ref. 4. Values are taken from Table III.

minimum energy of the *same* Hamiltonian.

The orbital eigenvalues presented in Table II were computed using the Ξ wave functions obtained by the solution of Eq. (12), but using the HF expression for the eigenvalue as explained in Ref. 8. These values are compared with the HF values and with those using the theoretical TW potential $V^{\mathrm{ex}}(\Xi_{\mathrm{TW}})$ as well as the original unmodified potential $V^{\mathrm{ex}}(\Xi_G)$ of Ref. 4. Some of the representative orbital eigenvalues calculated by the different methods are compared diagrammatically in Figs. 3(a) and 3(b). It is clear that the present $V^{\mathrm{ex}}(\Xi)$ potential is a substantial improvement over the other two previously used potentials since the Ξ eigenvalues are now consistently closer to the HF values.

Table III presents the total energy of the ground-state multiplets of various atoms calculated with the Ξ wave functions and the HF Hamiltonian. Some of the typical results of Table III are shown in Fig. 4. Here again the superiority of the present $V^{\mathrm{ex}}(\Xi)$ potential is obvious.

In conclusion, the exchange potential of the present Ξ method appears to be a very close *ab initio* local-density representation of the HF exchange potential.

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[1] J. C. Slater, Phys. Rev. 81, 385 (1951).

[2] J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1974), Vol. 4.

[3] M. S. Gopinathan, M. A. Whitehead, and R. Bogdanovic, Phys. Rev. A 14, 1 (1976).

[4] M. S. Gopinathan, Phys. Rev. A 15, 2135 (1977).

[5] T. J. Tseng and M. A. Whitehead, Phys. Rev. A 24, 16 (1981).

[6] T. J. Tseng and M. A. Whitehead, Phys. Rev. A 24, 21 (1981).

[7] B. Maessen and P. C. Schmidt, Theor. Chim. Acta 59, 299 (1981).

[8] M. S. Gopinathan and G. R. Rao, Phys. Rev. A 22, 1764 (1980).