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Dependence of the one-electron eigenvalues, ϵ_i, and the total energy, E, on the α parameter in the Hartree-Fock-Slater scheme for atoms

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The dependence of the one-electron eigenvalues and the total energy on the value of the parameter α in the Hartree-Fock-Slater (HFS) theory is considered. When the HFS wave function is used in the HFS Hamiltonian and in the Hartree-Fock Hamiltonian (HF) different trends occur. When the Latter correction to the wave function is used, different results are obtained. $E^{\mathrm{HF}}(\alpha_{\mathrm{HF}})$ is lower when Latter's correction is not used, and $E^{\mathrm{HF}}(\alpha_{\mathrm{ta}})$ is lower when it is used. Use of the α_{ta} of Gopinathan *et al.* given better ionization energies compared to experiment. No unique "best" α can be chosen.

I. INTRODUCTION

The Hartree-Fock-Slater (HFS) scheme[1] simplifies solution of the Hartree-Fock (HF) equations by replacing the exchange integrals with an averaged universal potential, proportional to the $\frac{1}{3}$rd power of the local charge density ρ. The proportionality constant α has been determined by several different methods.[2-6]

The α parameter of Schwarz, α_{HF},[4] is determined by setting the Hartree-Fock-Slater statistical total energy $E^{\mathrm{HFS}}(\alpha)$ [Eq. (11)] equal to the configuration-averaged HF energy (E^{HF}) reported by Mann.[7] The main difference between the $E^{\mathrm{HFS}}(\alpha)$ and the E^{HF} lies in the respective exchange energies.

Assuming a linear variation of the Fermi-hole density, Gopinathan *et al.*[5] proposed a set of theoretical α parameters (α_{ta}): If $n_\uparrow$ is the number of spin-up electrons then

$$\alpha_{\mathrm{ta}\uparrow}=\frac{8}{27}\left(\frac{4\pi^2}{3}\right)^{1/3}\frac{1/n_\uparrow+\frac{1}{2}}{(1/n_\uparrow+\frac{1}{3})^{2/3}} \tag{1}$$

and for spin-down electrons,

$$\alpha_{\mathrm{ta}\downarrow}=\frac{8}{27}\left(\frac{4\pi^2}{3}\right)^{1/3}\frac{1/n_\downarrow+\frac{1}{2}}{(1/n_\downarrow+\frac{1}{3})^{2/3}}. \tag{2}$$

An average α is obtained from

$$\alpha_{\mathrm{ta}}=\frac{n_\uparrow\alpha_{\mathrm{ta}\uparrow}+n_\downarrow\alpha_{\mathrm{ta}\downarrow}}{n_\uparrow+n_\downarrow}. \tag{3}$$

(For closed-shell systems, $\alpha_{\mathrm{ta}}=\alpha_{\mathrm{ta}\uparrow}=\alpha_{\mathrm{ta}\downarrow}$.) Equation (1) can be rewritten as

$$\alpha_{\mathrm{ta}\uparrow}=c\,\frac{1/n_\uparrow+\frac{1}{2}}{(1/n_\uparrow+\frac{1}{3})^{2/3}}. \tag{4}$$

If $c=0.7275$, then Eq. (4) equals Eq. (1) as $n_\uparrow\to\infty$. However, for α_{HF}, the c value approaches 0.68 for large Z values. Therefore, a set of scaled α parameters was defined by

$$\alpha'_{\mathrm{ta}\uparrow}=0.68\,\frac{1/n_\uparrow+\frac{1}{2}}{(1/n_\uparrow+\frac{1}{3})^{2/3}} \tag{5}$$

and similarly for $\alpha'_{\mathrm{ta}\downarrow}$.

The exchange potential in the HFS scheme has an incorrect asymptotic behavior compared to the HF scheme. An *ad hoc* correction by Latter[8] modifies the tail of the HFS exchange potential so that it has the same asymptotic behavior as the HF exchange potential. The total energies calculated with this modification for the Mn^{+2} ion[9] and Ar atom[10] were higher than those calculated without the Latter modification.

The eigenvalues of the $X\alpha$ method do not obey Koopmans' theorem,[11] and the energy required to remove one electron from the kth orbital due to unrelaxed ionization is[12]

$$\begin{aligned} I_k^{ur} &\equiv I_k^{\mathrm{HFS}}(\alpha)\\ &=-\epsilon_k^{\mathrm{HFS}}(\alpha)+\tfrac{1}{2}\langle u_k^\alpha(1)u_k^\alpha(2)\,|g_{12}|\,u_k^\alpha(1)u_k^\alpha(2)\rangle+\cdots. \end{aligned} \tag{6}$$

When higher powers of ρ_k/ρ [where $\rho_k(1)=n_ku_k^2(1)$ and $\rho(1)=\sum_i n_iu_i^2(1)$] are included, I_k^{ur} becomes I_k^{ur} (exact), which is obtained from

$$\begin{aligned} I_k^{ur}\text{ (exact)} &\equiv I_k^{\mathrm{HFS}}(\alpha)\text{ (exact)}\\ &=E_+^{\mathrm{HFS}}(\alpha)-E_0^{\mathrm{HFS}}(\alpha). \end{aligned} \tag{7}$$

Thus I_k^{ur} (exact) $-\,I_k^{ur}$ gives the effect of the higher powers of ρ_k/ρ. Equation (7) defines the unrelaxed ionization potential, which is the total energy difference between the neutral atom energy and the energy of the ion calculated with the same unrelaxed orbitals which are obtained from the neutral atom $X\alpha$ calculations. Incidentally, the second term on the right-hand side of Eq. (6) is the self-interaction energy which is included in both the Coulomb energy integral and the exchange energy integral of the $X\alpha$ Hamiltonian H^{HFS}. When the self-interaction energy is properly considered, the eigenvalues calculated from the HFS equations obey Koopmans' theorem[12] as do the eigenvalues of the HF scheme, and the $X\alpha$ exchange potential has the same asymptotic behavior as the HF potential,[13] and the Latter modification is not required.

In this paper, the total energies and the one-electron energies for noble-gas atoms are investigated using the theoretically derived α parameters α_{ta} and α'_{ta}. By comparing these results to those calculated using the empirically parametrized α_{HF} values, we hope to find which α value would be best in atomic and molecular calculations.

II. METHOD

The nonrelativistic HFS one-electron Schrödinger equations are (energies in rydberg, distances in bohr)

$$\left(f_1 + \int \rho(2) g_{12} dr_2 + 2V_{X\alpha}(1)\right) u_i^\alpha(1) = \epsilon_i^{\mathrm{HFS}}(\alpha) u_i^\alpha(1) , \tag{8}$$

where

$$f_1 = -\nabla_1^2 - 2Z/r_1, \quad g_{12} = 2/r_{12} , \tag{9}$$

and

$$V_{X\alpha}(1) = -3\alpha[(3/8\pi)\rho(1)]^{1/3} . \tag{10}$$

The total HFS energy is

$$\begin{aligned} E^{\mathrm{HFS}}(\alpha) = {} & \sum_i n_i \langle u_i^\alpha(1) | f_1 | u_i^\alpha(1) \rangle + \sum_i \sum_j n_i n_j \langle u_i^\alpha(1) u_j^\alpha(2) | g_{12} | u_i^\alpha(1) u_j^\alpha(2) \rangle \\ & + \tfrac{3}{2} \sum_i n_i \langle u_i^\alpha(1) | V_{X\alpha}(1) | u_i^\alpha(1) \rangle . \end{aligned} \tag{11}$$

These $X\alpha$ orbitals u_i^α can be regarded as *approximate solutions of the* HF *one-electron equations*, so that $\epsilon_k^{\mathrm{HF}}(\alpha)$ is defined by

$$\epsilon_k^{\mathrm{HF}}(\alpha) = \langle u_k^\alpha(1) | f_1 | u_k^\alpha(1) \rangle + \sum_i n_i \langle u_k^\alpha(1) u_i^\alpha(2) | g_{12} | u_k^\alpha(1) u_i^\alpha(2) - u_i^\alpha(1) u_k^\alpha(2) \rangle \tag{12}$$

and the HF total energy using the $X\alpha$ orbitals is

$$E^{\mathrm{HF}}(\alpha) = \sum_i n_i \langle u_i^\alpha(1) | f_1 | u_i^\alpha(1) \rangle + \sum_i \sum_j n_i n_j \langle u_i^\alpha(1) u_j^\alpha(2) | g_{12} | u_i^\alpha(1) u_j^\alpha(2) - u_j^\alpha(1) u_i^\alpha(2) \rangle . \tag{13}$$

The virial coefficient is calculated in each $X\alpha$ calculation to check whether the calculated energies satisfy the virial theorem. When the theorem is not satisfied, the scaled energy is calculated, according to Löwdin's method[14]

$$E_\eta = \eta^2 T + \eta V , \tag{14}$$

where

$$\eta = -V/2T , \tag{15}$$

V is the total potential energy, and T is the kinetic energy of the atom considered.

Three methods of calculating the ionization energies are considered:

(1) $\epsilon_k^{\mathrm{HF}}(\alpha)$, the HF eigenvalue [Eq. (12)], is calculated using the $X\alpha$ wave function. Schwarz and Connolly[15] noted that the accuracy of the $X\alpha$ eigenfunctions is comparable with the double-zeta functions of Clementi[16] for calculating $E^{\mathrm{HF}}(\alpha)$ total energies. Consequently, the one-electron eigenvalues using the HF Hamiltonian and the $X\alpha$ wave functions may be good approximate ionization potentials

$$I_k^{\mathrm{HF}}(\alpha) \simeq -\epsilon_k^{\mathrm{HF}}(\alpha) . \tag{16}$$

The equality holds by Koopmans' theorem when the HF wave function is used.

(2) By neglecting terms containing higher powers of ρ_k/ρ in Eq. (6), $I_k^{\mathrm{HFS}}(\alpha)$ is

$$I_k^{\mathrm{HFS}}(\alpha) = -\epsilon_k^{\mathrm{HFS}}(\alpha) + \tfrac{1}{2}\langle k \| k \rangle , \tag{17}$$

where

$$\langle k \| k \rangle = \langle u_k^\alpha(1) u_k^\alpha(2) | g_{12} | u_k^\alpha(1) u_k^\alpha(2) \rangle \tag{18}$$

is used to give $I_k^{\mathrm{HFS}}(\alpha)$ as an approximated to I_k^{ur} (exact) [Eq. (7)].

(3) The linear least-squares fit of Gopinathan[12]

$$I_k^{\mathrm{HFG}}(\alpha) = -\epsilon_k^{\mathrm{HFS}}(\alpha) + (0.281\,75 \pm 0.004\,95)\langle k \| k \rangle - (0.0664 \pm 0.0543) \qquad (19)$$

is used. The ionization potential calculated by Eq. (19) includes part of the relaxation.[12] The relaxed ionization potential can be calculated using Eq. (7), in which the total energy of the ion $E_+^{\mathrm{HFS}}(\alpha')$ is calculated using orbitals which are the self-consistent-field (SCF) solutions of an $X\alpha$ calculation on the ion. The results from Eqs. (16) and (17) are the approximate unrelaxed ionization potentials.

III. RESULTS AND DISCUSSION

A modified Herman-Skillman SCF program[17] was used for the $X\alpha$ SCF calculations. The total energies were computed using Zare's integral program.[18] All computations were performed in double precision on an IBM 370/158. The one-electron energy criterion of self-consistency was set at 0.000 01 Ry.

Computations using the α parameters of Gopinathan *et al.*[5] and Schwarz[4] have been performed for the atoms He, Ne, Ar, and Kr. The total energies which correspond to SCF calculations made *without* the Latter tail modification are given in Table I. The corresponding one-electron energies are given in Table II (Ref. 20). The relative differences of the calculated one-electron energies with respect to the true HF results $(\Delta I/Z)(10)$ are plotted in Figs. 1(a)–1(f). The total energies and one-electron energies corresponding to SCF calculations in which the Latter tail modification[8] was used were also computed and are available from the authors.

TABLE I. Calculated ground-state energies $-E(\alpha)$ Ry (no Latter tail modification). $E_{sc}^{\mathrm{HF}}(\alpha_{\mathrm{HF}})$ reported by Schwarz and Connolly (Ref. 15) are 5.721 98 (He), 257.0676 (Ne), and 1053.5962 (Ar). $E_{\mathrm{lim}}^{\mathrm{HF}}$ reported by Mann (Ref. 7) are 5.723 36 (He), 257.0942 (Ne), 1053.6350 (Ar), and 5504.1086 (Kr).

E[b] / α[a]	$-E^{\mathrm{HF}}(\alpha)$	$-E^{\mathrm{HSF}}(\alpha)$	$-E^{\mathrm{expt}}$[c]
He			
α_{HF} (0.772 98)	5.721 75	5.723 36	5.808
α_{ta} (0.866 172)	5.720 27	5.972 07	
α'_{ta} (0.841 991)	5.721 26	5.906 93	
Ne			
α_{HF} (0.739 81)	257.066 3	257.094 0	257.8
α_{ta} (0.744 568)	257.066 7	257.459 2	
α'_{ta} (0.723 781)	257.065 9	256.861 7	
Ar			
α_{HF} (0.721 77)	1053.591 5	1053.630 4	1055.2
α_{ta} (0.734 031)	1053.591 2	1054.657 1	
α'_{ta} (0.713 538)	1053.596 2	1052.946 5	
Kr			
α_{HF} (0.705 74)	5504.006 4	5504.090 0	
α_{ta} (0.729 428)	5504.004 3	5510.394 9	
α'_{ta} (0.709 064)	5504.006 5	5504.974 3	

[a] α_{HF} (Schwarz, Ref. 4); α_{ta} and α'_{ta} (Gopinathan *et al.*, Ref. 5).

[b] E_η is given by Eq. (14): $E_\eta^{\mathrm{HF}}(\alpha'_{\mathrm{ta}})$ for He = 5.722 72, $E_\eta^{\mathrm{HF}}(\alpha_{\mathrm{ta}})$ for He = 5.722 91, and $E_\eta^{\mathrm{HF}}(\alpha_{\mathrm{ta}})$ for Kr = 5504.0061.

[c] Reference 19.

A. Total energies

It is seen (Table I) that $E^{\mathrm{HF}}(\alpha)$ [Eq. (13)] is almost independent of the set of α values used. All the $E^{\mathrm{HF}}(\alpha)$ are close to but higher than the HF limit.[7] The virial theorem holds in each set of calculated $T^{\mathrm{HFS}}(\alpha)$ and $V^{\mathrm{HFS}}(\alpha)$, but for $T^{\mathrm{HF}}(\alpha)$ and $V^{\mathrm{HF}}(\alpha)$, while using α_{HF} satisfies the virial theorem, α'_{ta} does not satisfy the theorem for He (1 part in 10^4 disagreement) and α_{ta} does not satisfy the theorem for He (1 in 10^3) and Kr (1 in 10^7). These results were scaled using Eq. (14) to give the $E_\eta^{\mathrm{HF}}(\alpha)$ in the footnote to Table I.

When the effect of different α's in the $X\alpha$ orbitals is ignored, Eqs. (10) and (11) predict $E^{\mathrm{HFS}}(\alpha)$ to be a linear function of α—the larger is α, the lower is $E^{\mathrm{HFS}}(\alpha)$. Thus $E^{\mathrm{HFS}}(\alpha_{\mathrm{ta}})$ is always the lowest $E^{\mathrm{HFS}}(\alpha)$ energy since α_{ta} is the largest among the three sets of α's considered for each atom. In He, $E^{\mathrm{HFS}}(\alpha_{\mathrm{ta}})$ and $E^{\mathrm{HFS}}(\alpha'_{\mathrm{ta}})$ are lower than the experimental value because the α_{ta} parameter is derived theoretically and therefore does not compensate for the error in $\rho^{1/3}$, whereas α_{HF} is determined by requiring that $E^{\mathrm{HFS}}(\alpha)$ equal the HF total energy[7] and does compensate (by design) for the error in $\rho^{1/3}$. Numerically, the self-interaction energy (V_i) is 2.089 03 Ry, and the statistical exchange correlation energy (V_{sexc}) is −2.340 83 Ry. The latter is lower by −0.2518 Ry than when the HF results are considered, where the exchange correlation energy (V_{exc}), with the true Hamiltonian, is zero for He. This is because the exchange energy V_{ex}, where $V_{\mathrm{ex}} = V_{\mathrm{exc}} + V_i$, equals the negative of the self-interaction energy $(-V_i)$ because they are the same integral. Consequently, the $E^{\mathrm{HFS}}(\alpha_{\mathrm{ta}})$ is too low because

$$E^{\mathrm{HFS}}(\alpha) = \langle f_1 \rangle + (V_c + V_i) + (V_{\mathrm{ex}} - V_i)$$
$$= \langle f_1 \rangle + (V_c + V_i) + V_{\mathrm{sexc}},$$

where V_c is the Coulomb energy and f_1 is defined in Eq. (9). The energy V_i in He is 36% of the $E^{\mathrm{HFS}}(\alpha_{\mathrm{ta}})$ and, while the percentage will decrease for heavier atoms, it will still be significant.

Therefore, with properly calculated V_i removed from the V_{sexc}, the true statistical exchange energy V_{sex} is left in the HFS Hamiltonian, and the $X\alpha$ method has to be reparametrized.[23]

When the Latter tail modification[8] is used, all the total energies $E^{\text{HF}}_{\text{Lat}}(\alpha)$ for the various α values are higher than the corresponding $E^{\text{HF}}(\alpha)$ calculated without the modification; the difference is at least $\simeq 0.03$ Ry for the cases reported here. The modification makes the $X\alpha$ orbitals have the same mathematical asymptotic behavior as the HF orbitals but as noted (Ref. 24) it is physically unrealistic as it produces a nonvanishing surface charge density on the cutoff sphere.

Similarly, $E^{\text{HFS}}_{\text{Lat}}(\alpha)$ (with the Latter modification) lies always above the corresponding $E^{\text{HFS}}(\alpha)$. This suggests that if $E^{\text{HFS}}_{\text{Lat}}(\alpha)$ is equal to $E^{\text{HF}}_{\text{limit}}$, the α value will exceed α_{HF}. For example we obtain α's of 0.782 66 for He and 0.731 617 for Ne compared to $\alpha_{\text{HF}}(\text{He}) = 0.772\,98$, and $\alpha_{\text{HF}}(\text{Ne}) = 0.730\,81$.

When the Latter modification is used, α_{ta} *always* gives a total energy $E^{\text{HF}}_{\text{Lat}}(\alpha)$ closest to the HF limit.[7] This supports the recent results of Gopinathan and Rao[25] who showed that the α_{ta} always gave lower energies. However, this behavior of the energy with α_{ta} disappears when the Latter modification is not used.

B. One-electron energies

The values of $I^{\text{HF}}_k(\alpha)$ for α_{HF}, α_{ta}, and α'_{ta} group together as do the values of $I^{\text{HFS}}_k(\alpha)$ and $I^{\text{HFG}}_k(\alpha)$, Table II, and Figs. 1(a)–1(f). The values of $I^{\text{HF}}_k(\alpha)$, $I^{\text{HFS}}_k(\alpha)$, and $I^{\text{HFG}}_k(\alpha)$ are well separated, but have parallel trends.

The values of the $I^{\text{HF}}_k(\alpha)$ group are normally closer to the true HF values I^{HF}_k except for the 2*p* level of Kr, where the $I^{\text{HFS}}_k(\alpha)$ are closer to I^{HF}_k. The $I^{\text{HFG}}_k(\alpha)$ values are usually further away from the I^{HF}_k but in several cases are closer to the experimental results. Specifically, within the group of $I^{\text{HF}}_k(\alpha)$ values, results calculated with α_{HF} are closest to the true HF values for all orbitals of He and Kr and for the 2*s* of Ne. Those calculated with α'_{ta} are closest to I^{HF}_k for the 1*s* of Ne and all orbitals of Ar. The set of α_{ta}, the theoretically derived α values, only gives the 2*p* of Ne closest to the true HF results, *but* $I^{\text{HF}}_k(\alpha_{\text{ta}})$ are always closest to the experimental results for all orbitals and all atoms reported here.

Among the group of $I^{\text{HFS}}_k(\alpha)$ values, results using α_{HF} give closer values to the true HF results I^{HF}_k for the 1*s* of He, the 2*s* of Ne, and the 1*s*, 3*d*, and 4*p* of Kr. For α'_{ta}, $I^{\text{HFS}}_k(\alpha'_{\text{ta}})$ of the 1*s* and 2*p* of Ne, the 1*s*, 2*p*, and 3*p* of Ar, and the 2*p* of Kr are closest to the I^{HF}_k values, whereas $I^{\text{HFS}}_k(\alpha_{\text{ta}})$, with α_{ta}, are closer to I^{HF}_k for the 2*s* and 3*s* of Ar, and the 2*s*, 3*s*, 3*p*, and 4*s* of Kr. In contrast to $I^{\text{HF}}_k(\alpha_{\text{ta}})$ the $I^{\text{HFS}}_k(\alpha_{\text{ta}})$ are in most cases furthest away from the experimental results, except for the 2*s* of Ne and Ar and the 3*s* of Kr.

For the $I^{\text{HFG}}_k(\alpha)$, none of the calculated results using α_{HF} is closest to the true HF result I^{HF}_k, nor is any calculated $I^{\text{HFG}}_k(\alpha_{\text{HF}})$ closest to the experimental value. The $I^{\text{HFG}}_k(\alpha'_{\text{ta}})$ only give the 1*s* of Ne and the 3*d* of Kr closest to the experimental results, but none of the $I^{\text{HFG}}_k(\alpha'_{\text{ta}})$ is closest to the true HF result I^{HF}_k. Within the $I^{\text{HFG}}_k(\alpha)$ group the $I^{\text{HFG}}_k(\alpha_{\text{ta}})$ are always the closest ones to the HF results I^{HF}_k for all orbitals and all atoms, and they are also closest to the experimental values except for the 1*s* of Ne and the 3*d* of Kr.

When the Latter modification is used, almost the same conclusions are obtained. Each set of calculated I's is well separated, the trend of each curve within the group is the same, and normally $I^{\text{HF}}_{k,\text{Lat}}(\alpha)$ are closer to the true HF results I^{HF}_k. Among the $I^{\text{HF}}_{k,\text{Lat}}(\alpha)$ group, once again α_{ta} always gives the closest result to the experimental value I^{expt}_k. However, α_{ta} does not make $I^{\text{HFG}}_{k,\text{Lat}}(\alpha_{\text{ta}})$ close

TABLE II. One-electron energies $-\epsilon$ and I, (no Latter tail modification).[a]

Orbital	α [b]	$-\epsilon^{\text{HFS}}_k(\alpha)$ [c]	$I^{\text{HFS}}_k(\alpha)$ [d]	$I^{\text{HFG}}_k(\alpha)$ [e]	$I^{\text{HF}}_k(\alpha)$ [f]	I^{HF}_k [g]	I^{expt}_k [h]
He	α_{HF}	1.1655	2.1832	1.6725	1.8432	1.8359	1.81
1*s*	α_{ta}	1.2868	2.3313	1.8090	1.8156		
	α'_{ta}	1.2548	2.2924	1.7731	1.8231		
Ne	α_{HF}	60.9175	66.8581	64.1986	65.4794	65.5455	63.88
1*s*	α_{ta}	61.0142	66.9581	64.2972	65.4315		
	α'_{ta}	60.8681	66.8071	64.1483	65.5039		
2*s*	α_{HF}	2.6293	3.7339	3.1346	3.8685	3.8610	3.54
	α_{ta}	2.6507	3.6667	3.1568	3.8513		
	α'_{ta}	2.6185	3.6297	3.1234	3.8773		
2*p*	α_{HF}	0.9710	1.9383	1.4496	1.7150	1.7010	1.59
	α_{ta}	0.9897	1.9599	1.4700	1.6983		
	α'_{ta}	0.9614	1.9272	1.4392	1.7235		

TABLE II. *(Continued.)*

Orbital	α [b]	$-\epsilon_k^{\rm HFS}(\alpha)$ [c]	$I_k^{\rm HFS}(\alpha)$ [d]	$I_k^{\rm HFG}(\alpha)$ [e]	$I_k^{\rm HF}(\alpha)$ [f]	$I_k^{\rm HF}$ [g]	$I_k^{\rm expt}$ [h]
Ar	$\alpha_{\rm HF}$	228.2473	239.1411	234.3196	237.0804	237.2213	234.88
1*s*	$\alpha_{\rm ta}$	228.4311	239.3276	234.5049	237.0185		
	$\alpha'_{\rm ta}$	228.1265	239.0184	234.1977	237.1244		
2*s*	$\alpha_{\rm HF}$	21.6717	23.8447	22.8298	24.5475	24.6449	23.95
	$\alpha_{\rm ta}$	21.7197	23.8941	22.8786	24.5150		
	$\alpha'_{\rm ta}$	21.6395	23.8116	22.7971	24.5693		
2*p*	$\alpha_{\rm HF}$	16.9746	19.4061	18.2783	19.0601	19.1435	18.46
Ar	$\alpha_{\rm ta}$	17.0242	19.4577	18.3290	19.0249		
	$\alpha'_{\rm ta}$	16.9415	19.3716	18.2445	19.0837		
3*s*	$\alpha_{\rm HF}$	1.7250	2.3658	2.0197	2.5367	2.5550	2.12
	$\alpha_{\rm ta}$	1.7386	2.3802	2.0337	2.5261		
	$\alpha'_{\rm ta}$	1.7159	2.3562	2.0103	2.5439		
3*p*	$\alpha_{\rm HF}$	0.7192	1.2677	0.9619	1.1659	1.1823	1.16
	$\alpha_{\rm ta}$	0.7310	1.2809	0.9745	1.1567		
	$\alpha'_{\rm ta}$	0.7112	1.2587	0.9533	1.1720		
Kr	$\alpha_{\rm HF}$	1021.0153	1043.1182	1033.4039	1040.1582	1040.3288	1033.89
1*s*	$\alpha_{\rm ta}$	1021.7781	1043.8863	1034.1696	1039.9328		
	$\alpha'_{\rm ta}$	1021.1227	1043.2263	1033.5117	1040.1265		
2*s*	$\alpha_{\rm HF}$	132.7705	137.5811	135.4148	139.6751	139.8059	136.57
	$\alpha_{\rm ta}$	132.9830	137.7959	135.6286	139.5148		
	$\alpha'_{\rm ta}$	132.8004	137.6113	135.4449	139.6526		
2*p*	$\alpha_{\rm HF}$	120.2602	125.8960	123.3696	125.8977	126.0193	123.78
	$\alpha_{\rm ta}$	120.4909	126.1300	123.6021	125.7283		
	$\alpha'_{\rm ta}$	120.2927	125.9290	123.4023	125.8739		
3*s*	$\alpha_{\rm HF}$	18.6336	20.2940	19.5028	21.6512	21.6987	21.10
	$\alpha_{\rm ta}$	18.7141	20.3761	19.5842	21.5702		
	$\alpha'_{\rm ta}$	18.6449	20.3055	19.5142	21.6398		
3*p*	$\alpha_{\rm HF}$	14.1741	15.8289	15.0402	16.6211	16.6628	15.67
	$\alpha_{\rm ta}$	14.2529	15.9097	15.1201	16.5396		
	$\alpha'_{\rm ta}$	14.1851	15.8402	15.0513	16.6097		
3*d*	$\alpha_{\rm HF}$	6.1351	7.7930	7.0029	7.6114	7.6503	7.03
	$\alpha_{\rm ta}$	6.2049	7.8663	7.0747	7.5290		
	$\alpha'_{\rm ta}$	6.1449	7.8033	7.0130	7.5999		
4*s*	$\alpha_{\rm HF}$	1.5806	2.1454	1.8325	2.2996	2.3057	1.87
	$\alpha_{\rm ta}$	1.6048	2.1709	1.8574	2.2776		
	$\alpha'_{\rm ta}$	1.5840	2.1490	1.8359	2.2965		
4*p*	$\alpha_{\rm HF}$	0.6313	1.0959	0.8267	1.0375	1.0482	1.01
	$\alpha_{\rm ta}$	0.6517	1.1186	0.8484	1.0204		
	$\alpha'_{\rm ta}$	0.6341	1.0990	0.8296	1.0352		

[a] Results with the Latter tail modification are not reported here; they are available on request.

[b] $\alpha_{\rm HF}$ (Schwarz, Ref. 4); $\alpha_{\rm ta}$ and $\alpha'_{\rm ta}$ (Gopinathan *et al.*, Ref. 5).

[c] $\epsilon_k^{\rm HFS}(\alpha)$ is the eigenvalue from Eq. (8): $\frac{1}{2}\langle k\|k\rangle = \left[I_k^{\rm HFS}(\alpha) + \epsilon_k^{\rm HFS}(\alpha)\right]$.

[d] $I_k^{\rm HFS}(\alpha)$ defined in Eq. (17).

[e] $I_k^{\rm HFG}(\alpha)$ defined in Eq. (19).

[f] $I_k^{\rm HF}(\alpha)$ defined in Eq. (16).

[g] $I_k^{\rm HF} = -\epsilon_k^{\rm HF}$; the eigenvalue from Eq. (12) but with HF orbitals; values were taken from Clementi (Ref. 16). For atoms considered, the HF total energies of Clementi differ from those of Mann (Refs. 7 and 15) in the seventh figure, so the eigenvalues of Clementi should be very close to those of Mann.

[h] From Slater (Ref. 22), subject to the relativistic correction calculated by Herman and Skillman (Ref. 17).

to the experimental value $I_k^{\rm expt}$, unlike its behavior without the Latter modification. For example, results of $I_{k,\rm Lat}^{\rm HFG}(\alpha_{\rm ta})$ for the 1*s* of He and Ne, the 2*p* and 3*s* of Ar, and the 3*d* and 4*s* of Kr are further away from $I_k^{\rm expt}$ compared to the $I_{k,\rm Lat}^{\rm HFG}(\alpha)$ with $\alpha_{\rm HF}$ or $\alpha'_{\rm ta}$. However, they are still closest to the HF results $I_k^{\rm HF}$ except for the 1*s* of He where $I_{k,\rm Lat}^{\rm HFG}(\alpha_{\rm HF})$ is the closest one.

IV. CONCLUSIONS

The conclusions are as follows:

(1) If the HF total energy is calculated using $X\alpha$ wave functions, then $E^{\mathrm{HF}}(\alpha)$ is almost independent of the α parameter. Specifically, the deviation is only a few parts in 1000 or less for various sets of α used in the present $E^{\mathrm{HF}}(\alpha)$ calculations. Consequently, all calculated $E^{\mathrm{HF}}(\alpha)$ values are close to, but lie above, the HF limit. If the Latter tail modification is used, $E^{\mathrm{HF}}_{\mathrm{Lat}}(\alpha)$ are generally shifted up, compared to $E^{\mathrm{HF}}(\alpha)$, by at least 0.03 Ry for atoms calculated in this work.

(2) Although no unique conclusion can be drawn as to which set of α values gives results closest to the true HF results I_k^{HF}, the $I_k^{\mathrm{HF}}(\alpha_{\mathrm{HF}})$, with α_{HF}, usually give a closer fit to I_k^{HF}.

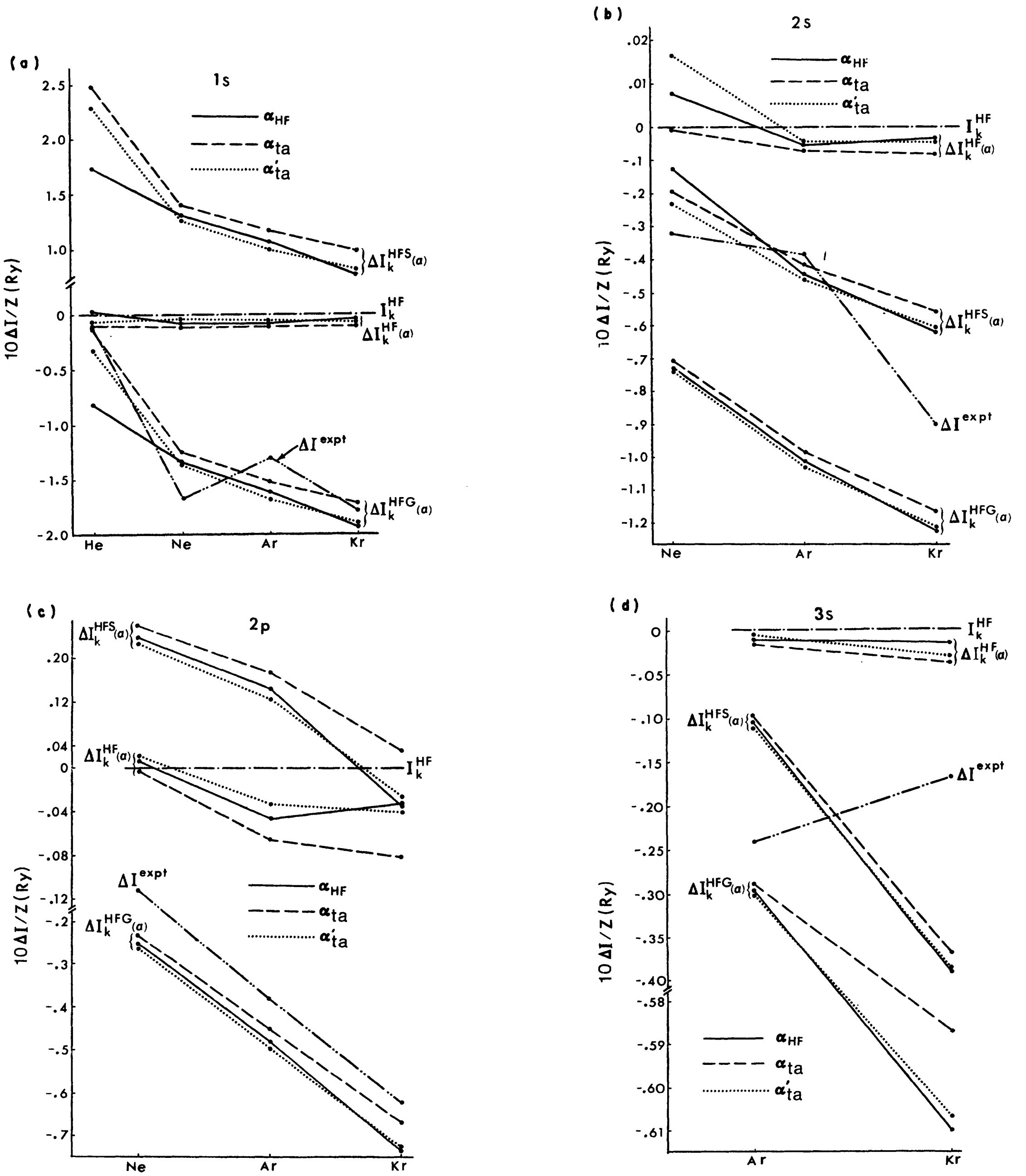

FIG. 1. Atomic ionization potentials calculated without the Latter tail modification for different α (α_{HF}, α_{ta} and α'_{ta}). Only the calculated $I_k^{\mathrm{HF}}(\alpha)$, $I_k^{\mathrm{HFS}}(\alpha)$, and $I_k^{\mathrm{HFG}}(\alpha)$ relative to the true HF result I_k^{HF} are plotted as $\Delta I_k^{\mathrm{HF}}(\alpha_{\mathrm{HF}}) = I_k^{\mathrm{HF}}(\alpha_{\mathrm{HF}}) - I_k^{\mathrm{HF}}$, etc. Then $(10\Delta I/Z)$ is plotted against Z for each orbital and against the $3d$, $4s$, and $4p$ orbitals for Kr.

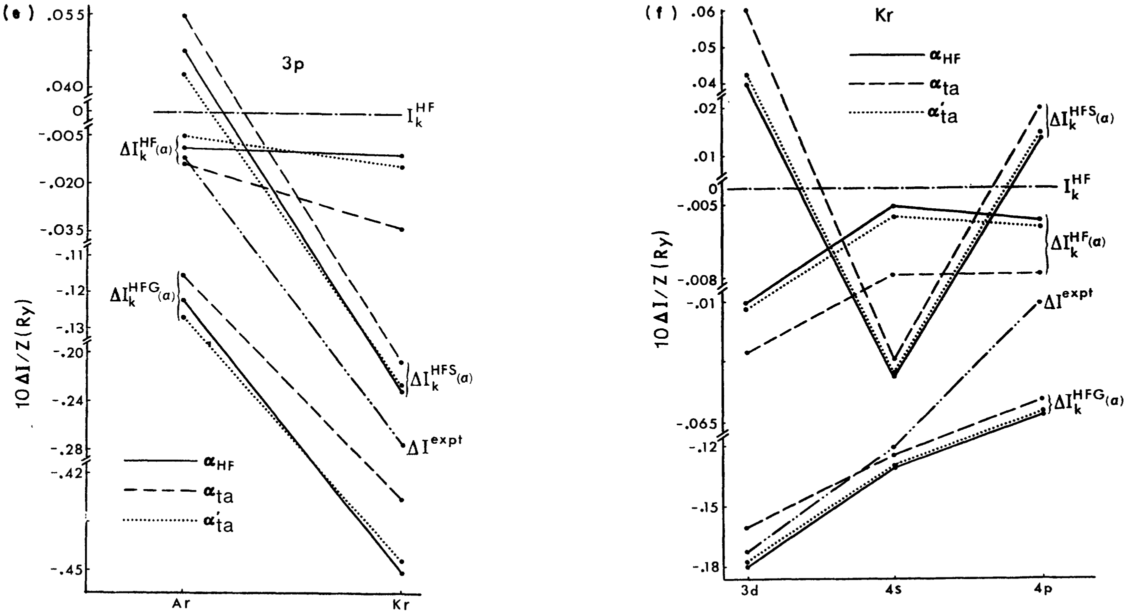

FIG. 1. *(Continued.)*

(3) The α_{ta}, in the group of $I_k^{HF}(\alpha)$ or $I_k^{HFG}(\alpha)$, generally give results closer to the experimental value I_k^{expt} than do other α values. It is hoped that when the self-interaction term is explicitly treated, then $E^{HFS}(\alpha_{ta})$ will no longer be lower than the experimental value. Consideration of the self-interaction energy is under study.[23]

Finally, in reporting $X\alpha$ calculations workers should make clear whether the Latter correction is or is not used, as quite different results are obtained without this correction. It will be interesting to study the change in E and ϵ with different α when the Coulomb hole correction is also included in the calculation.[26]

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[20] J. H. Wood kindly pointed out that, in Table II, a more

accurate unrelaxed I value can be calculated by

$$I_k^R(\alpha) = -\epsilon_k^{\mathrm{HFS}}(\alpha) + \tfrac{1}{2}\left[F^0(k,k) - 2\alpha\left(\frac{3}{8\pi}\right)^{1/3}\int \frac{\rho_k^2(1)}{[\rho(1)]^{2/3}}\,d\tau_1\right],$$

where F°, the $\langle k \| k \rangle$ term in Eq. (18), is the usual F integral (Ref. 21). Now, comparing with Eq. (17), it is seen that the second term in the brackets has been neglected, giving $I_k^{\mathrm{HFS}}(\alpha)$. Including this second term gives $I_k^R(\alpha)$: the differences (Table below) are a few hundredths of a Ry for the examples considered. The $I_k^R(\alpha)$ are, of course, close to ΔE_k^{ur} according to the definition [see Eq. (7)] or in the HHF method [Ref. 1(b)]:

$$\Delta E_k^{ur} = \langle E(q_k)\rangle - \langle E(q_k - 1)\rangle = \left.\frac{\partial\langle E\rangle}{\partial q_k}\right|_0 - \frac{1}{2}\left.\frac{\partial^2\langle E\rangle}{\partial q_k^2}\right|_0 + \cdots .$$

J. H. Wood also compared $I_k^{\mathrm{HFG}}(\alpha)$ [Eq. (19)] with the $\Delta E_k^{\mathrm{rel}}$ calculated by Eq. (7) or the above equation but with relaxed $X\alpha$ orbitals. The agreement between them should be noted.

Kr	$\Delta E_k^{ur}(\alpha)$	$I_k^R(\alpha)$	$I_k^{\mathrm{HFS}}(\alpha)$	$\Delta E_k^{\mathrm{rel}}(\alpha)$	$I_k^{\mathrm{HFG}}(\alpha)$
3*p*	15.7957	15.7962	15.8328	15.105	15.040
3*d*	7.7637	7.7640	7.7973	7.064	7.002
4*s*	2.1265	2.1271	2.1471	1.999	1.832
4*p*	1.0808	1.0812	1.0976	1.002	0.827

(Results were taken from J. H. Wood.)

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