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J-independent relativistic contributions to the s-d interconfiguration energies of the iron series: Some consequences for density-functional theory

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It has been found that, when the occupancy of the $3d$ orbital changes in the iron series (such as in s-d transfer and electron removal), the J-independent relativistic energy contributions (mass-velocity, one- and two-body Darwin, and electron-spin contact terms) to the corresponding energy differences are non-negligible. Thus they should be taken into account when a comparison of the calculated quantities with the experimental values is made for the purpose of testing the accuracy of a given theoretical approximation. In particular, the s-d interconfiguration energies and the removal energies are often used to test various approximations for exchange-correlation and correlation-energy functionals in density-functional theory. One of the conclusions of this study is that density-functional theory with its various approximations for the correlation-energy functional does not reproduce adequately the correlation-energy contributions to these energy differences for the iron-series elements.

I. INTRODUCTION

There have been many studies[1-4] of s-d interconfiguration energies (ICE's) since their introduction[1] as a measure of the adequacy of various approximations for the exchange-correlation-energy functional, $E_{xc}[n_\uparrow, n_\downarrow]$, in nonrelativistic density-functional theory (DFT). Of particular concern to the present work is that of Baroni,[4] who compared the theoretical results obtained from the local spin-density approximation (LSDA) for E_{xc} with those from an exact treatment of exchange, E_x, and a LSDA for the correlation-energy functional, $E_c[n_\uparrow, n_\downarrow]$ (referred to as LSDX in Ref. 4). Baroni concluded that the LSDX was superior to the LSDA. However, in all of the studies[1-4] the only account of possible relativistic effects in the experimental data was an averaging over the fine-structure splitting due to the spin-orbit coupling to produce the $(2J+1)$ weighted experimental ICE's (henceforth referred to as experimental ICE's or ΔE^{expt}) which are then used to judge the adequacy of the various DFT methods.

In a recent analysis[5] (henceforth referred to as LV88) of correlation-energy functionals it was found that when the occupancy of *a* $3d$ orbital changes the J-independent relativistic contributions (i.e., the mass-velocity term, the one- and two-body Darwin terms, and the electron-spin contact term) make non-negligible contributions to electron removal energies (RE's) for $3d$ transition-series elements and to s-d ICE's in V^+, Co^+, and Ni^+. In the present work these calculations are extended to the other positive ions and all the neutral atoms of the iron series. In most cases, the net result of these relativistic effects is to increase the magnitude of the semiempirical estimates for the correlation-energy contributions to these quantities. One of the unexpected consequences of the removal of the relativistic contribution from the experimental s-d ICE is to make the $3d^9 4s$ the nonrelativistic ground-state configuration for Ni. Thus, any stringent test of a nonrelativistic procedure for calculating correlation energies should take these relativistic contributions into account.

The presently available approximations for the $E_c[n_\uparrow, n_\downarrow]$ were examined in LV88 and were found to make serious errors for the correlation-energy contributions to electron RE's for the $3d$-series elements with Z between 22 (Ti) and 28 (Ni). These inadequacies were most pronounced for the electron affinities (EA's) of Fe, Co, and Ni (see Figs. 1 and 2 in LV88) where these correlation-energy functionals reproduce $\lesssim$ half of the semiempirical values. It is important to note that in contrast to the other elements considered in LV88, for Ti^-, V^-, Fe^-, Co^-, and Ni^- it is a $3d$ electron that is being removed. Thus, our conclusion was that the various approximations used for $E_c[n_\uparrow, n_\downarrow]$ are inadequate whenever the occupancy of the $3d$ orbital changes. One of the purposes of the present work is to point out that similar inadequacies occur when an electron is transferred from a s to a d orbital in neutral and positive ions. Hence, the above conclusion of LV88 can be generalized as follows: the approximate $E_c[n_\uparrow, n_\downarrow]$ presently in use fail to reproduce the correlation-energy contribution whenever a $3d$ orbital is directly involved in the removal or transfer of an electron. The errors are smaller for the first half of the $3d$-series elements where the spins of $3d$ electrons are all parallel and thus they are not strongly correlated. On the other hand, when the minority spin electron is being removed from or transferred to the $3d$ orbital in the second half of the series, the antiparallel pairs of $3d$ electrons contribute significantly to the correlation energy. It is for these elements that the inadequacy of the approximations is most apparent.

In LV88 and in the present investigation, it was the Hartree-Fock (HF) system method[6,7] (denoted by LSDX in Ref. 4) of the DFT that was used to include the correlation energies in the calculations of the total energies for

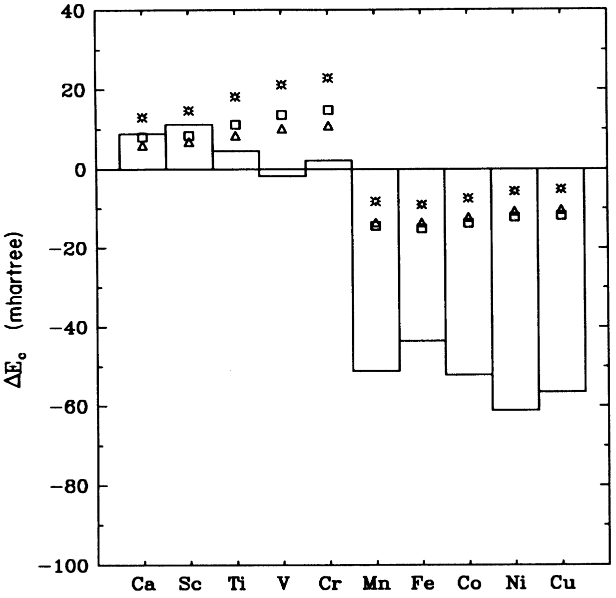

FIG. 1. The ΔE_c^{se} for *s-d* ICE's (bars) are shown for neutral atoms as indicated on the abscissa and are compared with the DFT correlation-energy contributions: KS is denoted by □, VW by $*$, and P by △.

the atomic systems considered. In this method the exchange energy is treated exactly by evaluating the Fock expression in terms of the single-particle wave functions and only the correlation-energy functional is approximated. An obvious criticism of this procedure is that it does not treat the exchange and the correlation energies in the same way (i.e., as explicit functionals of spin densities) as in the *s*-system method.[6] To compare these two methods, we have also calculated total energy differences using the HF kinetic, external, and Hartree energies and the LSDA for E_{xc} with the HF densities (referred to as the LSDA procedure). The rationale of this procedure is even if E_{xc} has a larger error than E_c when the LSDA is used for both of them, ΔE_{xc} could have a smaller error due to the cancellation of errors between ΔE_c and ΔE_x (which cannot occur in the HF-system method). It will be shown below that the accuracy of both procedures is similar, however the sign of the errors is opposite.

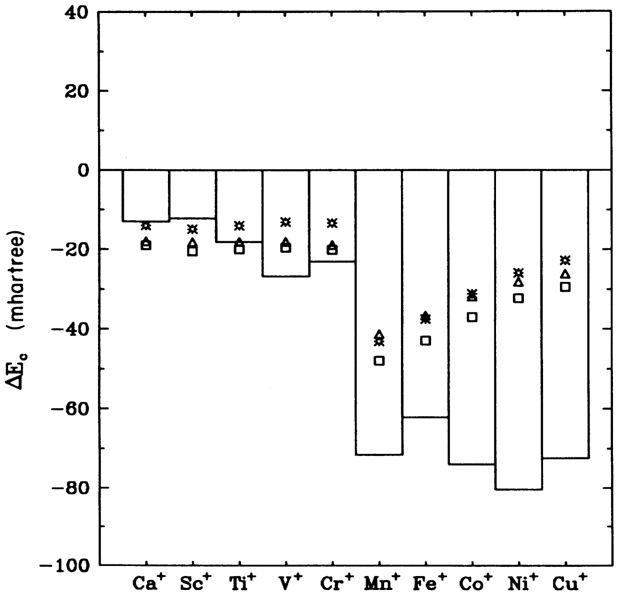

FIG. 2. The ΔE_c^{se} for *s-d* ICE's (bars) are shown for positive ions as indicated on the abscissa and are compared with the DFT correlation-energy contributions: KS is denoted by □, VW by $*$, and P by △.

In summary, this paper emphasizes three points: (i) The relativistic-energy contribution for the 3*d*-series atomic systems is in some cases of similar magnitude to the experimental *s-d* ICE's and should not be neglected when being used to investigate the role of correlation in producing the ground states and in testing various DFT approximations. (ii) DFT, with its various approximations for the correlation-energy functional, is not able to reproduce adequately the correlation-energy contribution to energy differences that involve the electron removal from or the electron transfer to a 3*d* orbital. The results are especially poor when the removed or transferred electron has a minority spin associated with it. (iii) When the exchange- and the correlation-energy functionals are treated in the same way by the LSDA procedure there is no significant improvement in the accuracy of the DFT results. In fact, the experimental results are bracketed by the HF-system method and the LSDA values.

II. PROCEDURE AND RESULTS

It is well known that accurate total correlation energies are difficult to obtain from either theoretical[8] or experimental investigations. A less ambitious but more feasible objective is to obtain the correlation-energy contributions to quantities like RE's and ICE's and perform the corresponding comparison between the experimental and theoretical values. Thus, the first problem is to isolate the correlation-energy contribution to the *s-d* ICE's and RE's. From a study of the experimental energies of the low-lying states[9,10] of atoms and ions with $Z \leq 30$, it is clear that a significant increase of the fine-structure splittings occurs when the 3*d* orbitals are occupied in the iron series. Thus, one should take into account the relativistic contributions in the semiempirical determination of the correlation-energy contribution. This is done by using the Breit-Pauli Hamiltonian[11,12]

$$\hat{H} = \hat{H}_{NR} + \hat{H}_R \ , \tag{1}$$

where $\hat{H}_{NR}$ is the usual nonrelativistic Hamiltonian that includes the kinetic, electron-nucleus, and electron-electron Coulomb interactions and $\hat{H}_R$ is the relativistic part which can be subdivided as follows:

$$\hat{H}_R = \hat{H}_{NF} + \hat{H}_F \ , \tag{2}$$

where $\hat{H}_{NF}$ and $\hat{H}_F$ correspond to the non-fine-structure

TABLE I. The $(2J+1)$ weighted experimental s-d ICE's for transition-series elements $(4s^23d^n \rightarrow 4s^13d^{n+1})$ are given in column two. The HF and relativistic-energy contributions (Ref. 13) to s-d ICE's are given in columns three and four, respectively. The semiempirical correlation-energy contributions to the ICE's are compared with the various approximations for correlation energy functionals as indicated. All energies are in mhartree.

Element	ΔE^{expt}	ΔE_{HF}	ΔE_{rel}	ΔE_c^{se}	ΔE_c^{KS}	ΔE_c^{VW}	ΔE_c^{P}
Ca	92.7	81	3	9	8	13	6
Sc	52.4	37	4	11	8	15	7
Ti	29.6	20	5	5	11	18	9
V	9.0	5	6	−2	14	21	10
Cr	−36.9	−47	7	3	15	23	11
Mn	78.8	122	8	−51	−14	−8	−14
Fe	32.1	66	10	−44	−15	−9	−14
Co	15.3	56	11	−52	−14	−7	−12
Ni	−1.1	47	13	−61	−12	−6	−11
Cu	−54.8	−14	15	−56	−12	−5	−11

and the fine-structure contributions, respectively. For our purposes it is adequate to treat $\hat{H}_{\text{R}}$ perturbatively with a single-configuration HF wave function. The effect of $\hat{H}_{\text{F}}$ is removed by performing a $(2J+1)$ average of the experimental energy levels. It should be pointed out that the spread in the experimental[9,10] J-dependent energies is, in fact, smaller than the effect of the J-independent terms for the systems under consideration. The contribution of $\hat{H}_{\text{NF}}$ to the total energy is calculated using the general HF program[13] which includes a perturbative evaluation of the mass-velocity, one- and two-body Darwin, and spin-contact terms [the orbit-orbit interaction is neglected since its contribution is usually less than 1 mhartree (Ref. 14)]. The results for the HF and the J-independent relativistic effects are given in Tables I and II where they are compared with the $(2J+1)$ weighted experimental energy differences. The relativistic-energy contributions, ΔE_{rel}, are taken into account in producing the semiempirical correlation-energy contributions, ΔE_c^{se} (i.e., $\Delta E_c^{\text{se}} = (s\text{-}d \text{ ICE or RE}) - \Delta E_{\text{HF}} - \Delta E_{\text{rel}}$, ΔE_{HF} are the HF energy differences[13]) which are also given in Tables I and II and are compared with the DFT values (to be discussed below).

An unexpected finding of LV88 was that the J-independent relativistic effects make non-negligible contributions to the electron RE's, such as ionization potentials (IP's) and EA's, of the iron series whenever there are changes in the occupancy of a $3d$ orbital. For example, when an electron is removed from the ground states of V, Co, and Ni (to produce the ground states of V^+, Co^+, and Ni^+ the $4s$ orbitals are emptied with one electron being transferred to a $3d$ orbital), the relativistic contributions to their IP's are 9.2, 15.9, and 18.2 mhartree, respectively. On the other hand when a $3d$ electron is removed from Ti^-, V^-, Fe^-, Co^-, and Ni^- the relativistic contributions to their EA's are of similar magnitude but of opposite sign, i.e., −5.4, −6.6, −9.6, −11.1, and −12.8 mhartree, respectively. In contrast, the relativistic contribution to the EA's of all the other systems (including Cr^- and Cu^-) is less than 1 mhartree. Similarly for the ICE's presented in Tables I and II, one observes that the ΔE_{rel} is non-negligible and in V, Co, Ni, Ti^+,

TABLE II. The $(2J+1)$ weighted experimental s-d ICE's for transition-series positive ions $(4s^13d^n \rightarrow 3d^{n+1})$ are given in column two. The HF and relativistic-energy contributions (Ref. 13) to s-d ICE's are given in columns three and four, respectively. The semiempirical correlation-energy contributions to the ICE's are compared with the various approximations for correlation-energy functionals as indicated. All energies are in mhartree.

Ion	ΔE^{expt}	ΔE_{HF}	ΔE_{rel}	ΔE_c^{se}	ΔE_c^{KS}	ΔE_c^{VW}	ΔE_c^{P}
Ca^+	62.4	72	4	−13	−19	−14	−18
Sc^+	22.4	29	5	−12	−21	−15	−18
Ti^+	4.9	16	7	−18	−20	−14	−18
V^+	−13.3	6	8	−27	−20	−13	−18
Cr^+	−55.9	−42	10	−23	−20	−13	−19
Mn^+	66.4	128	10	−72	−48	−43	−41
Fe^+	11.0	62	12	−62	−43	−38	−37
Co^+	−18.4	42	13	−74	−37	−31	−32
Ni^+	−42.6	23	14	−82	−32	−26	−28
Cu^+	−103.2	−47	16	−72	−30	−23	−26

and Fe$^+$ it is of the same size as $\Delta E^{\rm expt}$. Moreover, we have found that in most cases considered the sign of the relativistic-energy contribution is such that it increases the estimated semiempirical correlation-energy contribution.

In all cases (see Tables I and II) the *J*-independent relativistic contributions tend to stabilize $3d^n4s^2$ versus $3d^{n+1}4s$ and $3d^n4s$ versus $3d^{n+1}$ configurations. For example, in cases such as V$^+$, Co$^+$, and Ni$^+$, the correlation-energy contribution must overcome an appreciable HF and relativistic bias for the $3d^n4s$ configurations to produce the correct ground-state configurations $3d^{n+1}$ (see LV88). Another important consequence of this effect is that when the relativistic contributions are removed from the experimental *s-d* ICE's, the ground state of $\hat{H}_{\rm NR}$ for Ni is $3d^94s$ (i.e., not the experimental ground state $3d^84s^2$). Similarly, the corresponding occupancies of the 3*d* and 4*s* orbitals produce nearly degenerate nonrelativistic energy levels in V, Co, Ti$^+$, and Fe$^+$ (i.e., $\{3d^44s$ and $3d^34s^2\}$, $\{3d^84s$ and $3d^74s^2\}$, $\{3d^3$ and $3d^24s\}$, and $\{3d^7$ and $3d^64s\}$, respectively).

Next, the question of how well the various DFT methods describe these correlation effects is addressed. The relevant aspects of the implementation of DFT are summarized in LV88 and will not be repeated here except for a few very brief comments. Namely with respect to the HF-system method, one notes that it is based on the standard HF approximation. In this procedure, it is assumed that the true ground-state spin densities can be represented by a single determinant HF-like wave function. Then the correlation-energy functional is defined as

$$E_c[n^{\uparrow},n_{\downarrow}]=F[n_{\uparrow},n_{\downarrow}]-F^{\rm HF}[n_{\uparrow},n_{\downarrow}] \ , \qquad (3)$$

where $F^{\rm HF}[n_{\uparrow},n_{\downarrow}]$ is the HF functional which contains the kinetic, classical Coulomb, and exchange energies. $F^{\rm HF}[n_{\uparrow},n_{\downarrow}]$ is unknown, however the usual HF approximation is variationally based and thus DFT theorems[15] apply to it. In this way, the HF-system method leads to the HF single-particle equations with an additional correlation potential. Because we are considering the *s-d* ICE's as well as the RE's the usual ground-state DFT is generalized to the lowest-energy states of specified symmetry.[16] The various approximations used for the $E_c[n_{\uparrow},n_{\downarrow}]$ are discussed in LV88 (see Ref. 17). In Tables I and II the semiempirical correlation-energy contributions are given and are compared with the theoretical values obtained from the KS, VW, and P approximate correlation-energy functionals.[17] (This work will consider only three of the functionals, i.e., KS, VW, and P, since it was found in LV88 that the SPP underestimates the correlation-energy contributions while the LMPH tends to overestimate the correlation-energy contributions except in the special cases of 3*d* transition series elements where there is no significant improvement.) It should be noted that for practical reasons and consistency, we have calculated the exchange-correlation and the correlation-energy functionals using the numerically determined HF spin densities.[13] As was pointed out in LV88, this approach introduced errors of ~1 mhartree and thus these errors can be ignored for our purposes. Also as in LV88, in all cases the spin densities were evaluated for the single determinant $M_L=L$ and $M_S=S$ state (L and S are the total orbital and spin angular momenta, respectively) without averaging over angles.

It is known[1,4] that conventional HF theory gives a poor description of the ICE's. In fact when the relativistic corrections are included the results are even worse. Thus it can be seen from Tables I and II that neglecting the relativistic corrections can sometimes lead to erroneous conclusions concerning the accuracy of the theory being tested. For example, from LV88, in the case of EA's the magnitude of the calculated correlation-energy contribution is ~2 to 4 times larger than the magnitude of the relativistic-energy contribution and their respective signs are opposite. For IP's, the correlation- and relativistic-energy contributions are of similar magnitudes and of the same sign. In the case of *s-d* ICE's for the neutral atoms the magnitudes for the calculated correlation- and relativistic-energy contributions are similar and in the second half of the 3*d* series of opposite sign thus nearly cancelling each other. For the positive ions the calculated correlation-energy contribution is of opposite sign and is approximately twice as large as the relativistic contribution. Thus, the better agreement of the HF system method results for *s-d* ICE's (in contrast to LSDA or pure HF values) with the experiment as observed, e.g., by Baroni[4] is somewhat misleading since the relativistic-energy contributions were not included.

From Tables I and II, it can be seen that when the correlation-energy contribution is added to the $\Delta E_{\rm HF}$ and $\Delta E_{\rm rel}$, the correct ground states are obtained in all cases except for Co$^+$ and Ni$^+$ (see LV88). On the other hand, the *s-d* ICE's are reproduced poorly especially for the atoms form Mn to Cu. This inadequacy is emphasized by the plots in Figs. 1 and 2 where the calculated ΔE_c are

TABLE III. Comparison of the LSDA and the HF-system method (KS) results with the "experimental" RE's. The *J*-independent relativistic contributions to RE's are subtracted out from all values given in this table. The deviations from the observed values are shown in parentheses. Energies are in mhartree.

Element	Expt.	KS	LSDA
		EA	
Ti	8.3	−6.6(−14.9)	26.4(18.1)
V	25.9	4.5(−21.4)	51.4(25.5)
Fe	15.6	−27.8(−43.4)	24.3(8.7)
Co	35.6	−16.7(−52.1)	55.7(20.3)
Ni	55.3	−6.1(−61.4)	84.6(29.3)
N[a]	41.0	28.5(−12.5)	36.5(−4.5)
		IP	
V	238.5	243.1(4.6)	217.1(−21.4)
Co	272.9	296.5(23.6)	261.7(−11.2)
Ni	262.4	293.9(31.5)	243.2(−19.2)
Ni[a]	276.6	259.1(−17.5)	291.3(14.7)

[a]The electron configuration for the neutral Ni was taken as $3d^94s$ (in contrast to $3d^84s^2$ as was done in the preceding line) and the corresponding RE's were adjusted to take account of this fact.

compared with ΔE_c^{se} for s-d ICE's. It should be noted from these figures that the errors in the calculated ΔE_c are approximately constant in the first and second half of the $3d$ transition series and are particularly large in the second half. We conclude from Figs. 1 and 2 and Tables I and II (also Table III in LV88) that none of the approximations for the correlation-energy functional reproduces the magnitude of the abrupt change in ΔE_c^{se} that occurs between Cr and Mn for neutral atoms and Cr^+ and Mn^+ for positive ions very accurately. In fact, for the RE's and s-d ICE's whenever an electron is removed from or transferred to the $3d$ orbital, in general, slightly better results are given by the KS form for the correlation-energy functional, i.e., not the gradient or self-interaction corrected functionals.

It could be argued that the large discrepancies seen in Figs. 1 and 2 could be due to the fact that it is the symmetry-dependent ground-state formalism of the DFT that is being used to calculate s-d ICE's and thus $E_c[n_\uparrow,n_\downarrow]$ should be explicitly symmetry dependent.[16] However, it can be observed from Fig. 3 where the calculated ΔE_c are compared with ΔE_c^{se} for EA's which involve strictly ground-state symmetry-independent DFT that the same type of inadequacy for the correlation-energy contribution to EA in the second half of the $3d$ series elements persists. Thus one cannot use the symmetry dependence of $E_c[n_\uparrow,n_\downarrow]$ as an excuse for the failure of these various approximate functionals.

In Tables III–V, the comparison is made between the HF-system method (KS) and the LSDA and the experimental RE's (Ref. 18) and s-d ICE's. The J-independent relativistic-energy contributions are subtracted out from the $(2J+1)$ weighted experimental values (denoted by "Expt." in Tables III–V) and are not included in the HF-system method or the LSDA results. It can be observed from these tables that while the HF-system method with the various approximations for $E_c[n_\uparrow,n_\downarrow]$ underestimates the EA's for the above elements, the LSDA procedure overestimates them. The opposite is true for the IP's of V, Co, and Ni. For the IP's of Co and Ni the LSDA procedure gives more accurate results than the HF-system method while for the IP of V it is the HF-system method that produces a better value. For the EA's of Fe, Co, and Ni, the LSDA gives closer agreement with experiment than the HF-system method (errors are of similar magnitude for the EA's of Ti and V). However, the fact that the LSDA overestimates the EA's makes this procedure less useful when it is used for predicting the possible stability of the negative ions.[19,20] Also because the local exchange-correlation energy functional does not completely cancel the Coulomb self-interaction

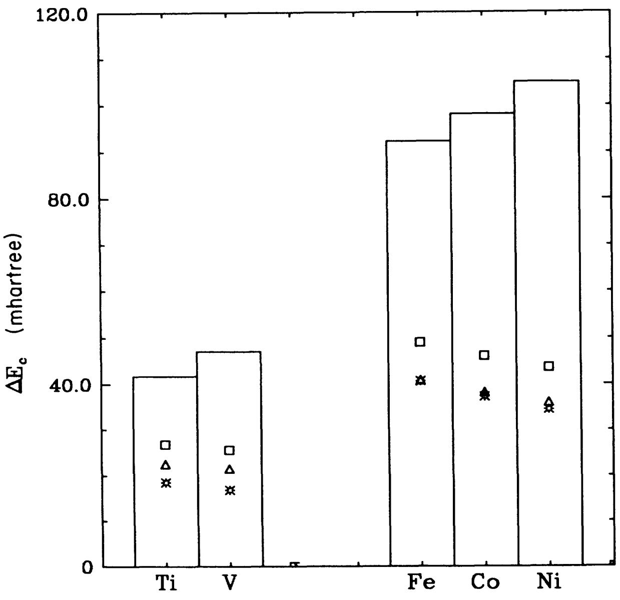

FIG. 3. The ΔE_c^{se} for EA's (bars) are shown for elements as indicated on the abscissa and are compared with the DFT correlation-energy contributions: KS is denoted by □, VW by $*$, and P by △.

TABLE IV. Comparison of the LSDA and the HF-system method (KS) results with the "experimental" s-d ICE's. The J-independent relativistic contributions to s-d ICE's are subtracted out from all values given in this table. The deviations from the observed values are shown in parentheses. Energies are in mhartree.

Element	Expt.	KS	LSDA
Ca	89.7	88.9(−0.8)	64.3(−25.4)
Sc	48.1	45.3(−2.8)	20.7(−27.3)
Ti	24.4	31.0(6.6)	−10.7(−35.0)
V	2.9	18.3(15.4)	−39.4(−42.3)
Cr	−44.3	−31.7(12.6)	−81.9(−37.6)
Mn	71.2	107.9(36.7)	44.8(−26.4)
Fe	22.6	51.0(28.4)	−0.4(−23.0)
Co	3.6	41.9(38.3)	−25.9(−29.5)
Ni	−14.2	34.7(48.9)	−48.1(−33.9)
Cu	−70.5	−25.7(44.8)	−93.7(−23.2)

TABLE V. Comparison of the LSDA and the HF-system method (KS) results with the "experimental" s-d ICE's. The J-independent relativistic contributions to s-d ICE's are subtracted out from all values given in this table. The deviations from the observed values are shown in parentheses. Energies are in mhartree.

Ion	Expt.	KS	LSDA
Ca^+	58.3	52.5(−5.8)	47.2(−11.1)
Sc^+	17.0	8.7(−8.3)	10.3(−6.7)
Ti^+	−1.7	−3.5(−1.8)	−14.9(−13.2)
V^+	−21.2	−13.9(7.3)	−38.2(−17.0)
Cr^+	−65.4	−62.5(2.9)	−76.7(−11.3)
Mn^+	56.4	80.0(23.6)	53.4(−3.0)
Fe^+	−0.7	18.5(19.2)	−4.7(−4.0)
Co^+	−31.9	5.0(36.9)	−41.6(−9.7)
Ni^+	−57.1	−8.9(48.2)	−76.2(−19.1)
Cu^+	−119.7	−76.7(43.0)	−133.3(−13.6)

in the Hartree energy (in the HF-system method there is a complete cancellation of the self-Coulomb interaction in the Hartree energy and the exchange energy), this procedure leads to incorrect large-r behavior of the effective potential in the single-particle equations (see, e.g., Ref. 21). As a consequence, the self-consistent-field solutions within the LSDA procedure do not, in general, exist for negative ions. For the s-d ICE's, the LSDA procedure underestimates whereas the HF-system method usually overestimates them the errors being of similar magnitude (in general the HF-system method produces better results for the first half of the iron series and the LSDA procedure is more accurate for the second half). Thus, there is no obvious advantage for using the LSDA over the HF-system method for atomic systems since accurate numerical HF procedures are readily available.[13] In fact when the correlation potential is essential for producing self-consistent converged solutions as is the case for some negative ions[19,20] there are advantages in using the HF-system method.

From this study, it is concluded that when an electron is removed from or transferred to the $3d$ orbital the relativistic-energy contribution should be included. In fact the inclusion of this contribution in general improves the agreement of the LSDA procedure with the experimental values for RE's and s-d ICE's. In many cases, the LSDA procedure and HF-system method results bracket the experimental values.

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