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Excitation energies, electron affinities and ionization potentials of the transition metals V, Cr and Mn

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Abstract. Configuration interaction calculations were carried out for neutral ground and excited states and positively and negatively ionized states of the V, Cr and Mn atoms. Energy convergence with respect to systematic expansion of both the one-electron and configuration bases was investigated for valence correlation. Contributions from core electrons to the differential correlation energies and relativistic effects were evaluated separately. Assuming additivity of these contributions, excitation energies, electron affinities and ionization potentials of the atoms were obtained. All calculated values were in excellent agreement with the observed values within a deviation of 0.056 eV except for the electron affinity of the V atom, which had a calculated value 0.110 eV larger than the experimental value.

Key words: Excitation energy – Electron affinity – Ionization potential – Energy convergence – Transition-metal atoms

1 Introduction

Considerable efforts have been made to accurately determine the low-lying excitation energies, ionization potentials (IPs) and electron affinities (EAs) of the first transition-metal atoms [1–22]. In order to calculate the energy difference between two states accurately, the total energies, and thus the differential correlation energies, must be calculated with equivalent accuracy for the two states. Equivalent description of the two states possessing different numbers of electrons, which is necessary for the calculations of IPs and EAs, is one of the fundamental difficulties in computational chemistry. Correlation of the electrons outside the Ar-like closed-shell core, which we call valence correlation, may make a major contribution to the energy difference; however, inclusion of core effects, i.e., core–valence and core correlation, is necessary to obtain an accurate energy difference. Especially when the two states possess different numbers of $3d$ electrons, as is often the case with transition-metal atoms, the core effects are essential, since the $3d$ electrons interact with the core electrons much more strongly than the $4s$ or $4p$ electrons do. To our knowledge, however, there has been a dearth of systematic studies that have considered both the one-electron and configuration bases, and particularly of such studies including the core effects.

In a previous article [23], the lowest $3d^n4s^2 \rightarrow 3d^{n+1}4s$ excitation energies, EAs, and IPs from the $4s$ and $3d$ subshells were studied for the Sc and Ti atoms by the configuration interaction (CI) method including the core effects. In Ref. [23], valence, core–valence and core correlation energies were calculated separately and the energy convergence with respect to both the one-electron and configuration bases was investigated. The valence-correlation energy was evaluated by obtaining a limit of full CI for the valence electrons, which we call the valence-full CI. The core–valence and core correlation energies were evaluated by restricted multireference single and double excitation CI (MRSDCI) calculations, whose configuration bases were composed of configuration state functions (CSFs) generated by simultaneous excitations of the core and valence electrons and those generated by double excitations of the core electrons, respectively. The relativistic effects were also estimated by carrying out Dirac–Fock calculations. By assuming the additivity of these contributions, the excitation energies, EAs and IPs of the Sc and Ti atoms were calculated in good agreement with the observed values.

Here, the same approach is applied to obtain the excitation energies, EAs and IPs of the V, Cr and Mn atoms. These results are expected to provide useful reference points for future molecular calculations.

In the next section, we describe the calculational procedure. The results and discussion are given in Sect. 3 and the final section contains the conclusions of this study.

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2 Method of calculation

Calculations were carried out on the following states of the respective atomic species:

V^+: $3d^4\ ^5D$, $3d^3 4s\ ^5F$; V: $3d^3 4s^2\ ^4F$, $3d^4 4s\ ^6D$; V^-: $3d^4 4s^2\ ^5D$; Cr^+: $3d^5\ ^6S$, $3d^4 4s\ ^6D$; Cr: $3d^5 4s\ ^7S$, $3d^4 4s^2\ ^5D$; Cr^-: $3d^5 4s^2\ ^6S$; Mn^+: $3d^5 4s\ ^7S$, $3d^4 4s^2\ ^5D$; Mn: $3d^5 4s^2\ ^6S$, $3d^6 4s\ ^6D$.

As is well known, the ground-state configuration of the first transition-metal atoms is $3d^n 4s^2$ in general, whereas that of Cr is $3d^5 4s$. Thus, the lowest $3d^n 4s^2 \rightarrow 3d^{n+1} 4s$ excitation energy was calculated for the V and Mn atoms, but the lowest $3d^{n+1} 4s \rightarrow 3d^n 4s^2$ excitation energy was calculated for the Cr atom. The lowest ionized state of the first transition-metal atoms is usually generated by the ionization of the 4*s* electron, as is the case for Cr and Mn; the lowest state of V^+ is, however, experimentally known to be $3d^4\ ^5D$. Therefore, we calculated $3d^4\ ^5D$ instead of $3d^2 4s^2$, which lies far above $3d^3 4s\ ^5F$. Finally, we did not carry out any calculations on the Mn^- ion, since the ground state of the Mn atom has the half-filled electronic structure of $3d^5 4s^2$ and does not have a positive EA.

The CI calculations were performed with full atomic symmetry using the program ATOMCI [24, 25]. Since ATOMCI follows a nonrelativistic formula, the relativistic effects were estimated by carrying out Dirac–Fock calculations using the program GRASP2 [26]. All the calculations were carried out on an IBM/RS6000 system.

2.1 Basis set

The basis set used in the present calculations was composed of Slater-type functions (STFs) with *l* values ranging from 0 to 5. The 1-2*s* and 2*p* STFs of Clementi and Roetti [27] were augmented with even-tempered sets [28–30] of 3*s*, 3*p*, 3*d*, 4*f*, 5*g* and 6*h* with a ratio of $\sqrt{2}$. The orbital exponents of 1-2*s* and 2*p* STFs optimized for the ground state of the neutral atom were also used for the negatively ionized state.

The exponents of the first 3*s* and 3*p* STFs were set to be the same as those of the outermost 2*s* and 2*p* STFs, respectively. We used the exponent of the outermost 2*p* STF also for the first 3*d* STF. In order to determine the size of the *s*-*d* even-tempered set, we repeated MRSDCI calculations with the *s*-*d* set, while increasing STFs until the energy lowering due to an additional STF was less than 1.0×10^{-5} au. In these calculations, we considered only the valence correlation with the reference space that consists of the Hartree–Fock (HF) configuration and those generated by the excitations of $4s^2 \rightarrow 4p^2$ and $3d^2 \rightarrow 4d^2$; this reference space is referred to as the minimal-reference space hereafter. The orbital exponents of the 4*f*, 5*g* and 6*h* STFs were chosen so that they cover the same radial extent as the 3*d* STFs do, i.e., $\zeta_{nl} = \frac{(2n+1)}{5}\zeta_{3d}$ for $nl = 4f$, 5*g* and 6*h*, where ζ_{nl} and ζ_{3d} stand for the orbital exponents of the *nl* and 3*d* STFs, respectively.

The basis set was determined individually for each state using this procedure. The sizes of the basis sets thus determined were (9-15*s*, 9-12*p*, 7-10*d*, 7-10*f*, 7-10*g*, 7-10*h*), where large sets such as (14*s*, 12*p*, 10*d*, 10*f*, 10*g*, 10*h*) and (15*s*, 12*p*, 9*d*, 9*f*, 9*g*, 9*h*) were required for V^- and Cr^-, respectively.

2.2 Valence correlation

For each state, we repeated MRSDCI calculations with the minimal-reference space, while increasing the *l* value of the basis functions, i.e., using the *s*-*d*, *s*-*f*, *s*-*g* and *s*-*h* sets. At each step of the calculations, natural orbitals (NOs) were generated for use in subsequent steps. At the same time, energy contributions from the respective *l* functions, *f* to *h*, were calculated, and the residual contributions from $l \geq 6$ functions were extrapolated. In order to reduce the scale of the CI calculations, the NOs whose occupation number was less than 1.0×10^{-6} were discarded at each step. The errors due to this NO truncation were checked by comparing the CI energy by a truncated set with that by a full set.

Using this truncated NO set, we carried out a series of MRSDCI calculations, while adding configurations to the reference space that had the largest weight in the previous CI wavefunctions. The multireference analogue of Davidson's correction [31] (denoted as +Q) was also calculated. The calculated CI and CI + Q energies were plotted against the weight of reference space, *w*, and the full CI limit was obtained by extrapolating the curves to $w = 1$, where the CI and CI + Q energies should coincide with each other.

2.3 Core–valence and core correlation

The core effects, i.e., the core–valence and core correlation, were included by considering the excitations of the 3*s* and 3*p* electrons. The core–valence and core correlation energies were evaluated separately by restricted MRSDCI calculations, which are referred to as CV-CI and C-CI, respectively. The configuration basis of CV-CI was composed of the CSFs generated by simultaneous excitations of the core and valence electrons, while that of C-CI was composed of those generated by double excitations of the core electrons. Single excitations from the core were considered in CV-CI.

The minimal-reference CV-CI and C-CI calculations were repeated, while increasing the *l* value of the basis functions up to *h*. The contributions from $l \geq 6$ functions to the core–valence and core correlation energies were estimated by extrapolating the contributions from the respective *l* functions, *f* to *h*. At each step of the calculations, the external NOs were generated and selected to obtain an effective and compact orbital set and the errors due to the NO truncation were evaluated. Using the *s*-*h* NO set thus determined, we performed the minimal-reference CV-CI and C-CI calculations and evaluated the core–valence and core correlation energies as the difference between the CI and reference energies. As for the ^5D ionized state of Mn, however, we included the $3d^6$ and $3d^5 4s$ configurations in the reference space, since they also yield the ^5D states that lie below $3d^4 4s^2\ ^5D$.

The reference space could not be expanded sufficiently owing to limited computational resources. In Ref. [23], convergence of the calculated correlation energies was investigated with expansion of the reference space for Ti and Ti^-. By the minimal–reference calculations, the core–valence and core correlation energies were overestimated and underestimated, respectively, by around 0.003 au (Figs. 4, 5 in Ref. [23]).

2.4 Relativistic effect

The relativistic effects were evaluated as the difference between the HF and Dirac–Fock energies. In the relativistic calculations, all possible *jj* terms were calculated and averaged with the weight of multiplicity for an *LS* term.

3 Results and discussion

3.1 Various contributions

The excitation energies, EAs and IPs obtained at each level of calculation are summarized in Tables 1, 2 and 3 for V, Cr and Mn, respectively, together with the total energy of the ground state of the neutral atom. Each contribution can be obtained by subtracting the value in the row above from that in the row concerned.

3.1.1 Valence correlation

The contributions from the *g* and *h* functions to the valence correlation, which are neglected in most existing theoretical calculations, brought about rather small – but not negligible – modifications to the energy differ-

Table 1. The excitation energies, electron affinities (*EAs*) and ionization potentials (*IPs*) of the V atom (in eV). The total energies (+924 au) are given for the ^4F state

Calculation	Total energy	Excitation energy	EA	IP	
	$3d^3 4s^2\ ^4F$	$3d^4 4s\ ^6D$	$3d^4 4s^2\ ^5D$	$3d^4\ ^5D$	$3d^3 4s\ ^5F$
Multiconfiguration self-consistent field	−0.92495	0.330	−0.275	6.127	6.430
Valence correlation					
Minimal-reference single and double excitation configuration interaction					
s-d	−0.94245	0.504	0.159	6.485	6.769
s-f	−0.96334	0.304	0.350	6.493	6.871
s-g	−0.96640	0.301	0.372	6.503	6.899
s-h	−0.96710	0.298	0.378	6.504	6.905
Full configuration interaction limit	−0.96808	0.300	0.463	6.526	6.925
$l \geq 6$ functions[a]	−0.96844	0.301	0.466	6.527	6.929
Truncated natural orbitals[a]	−0.96852	0.301	0.466	6.528	6.930
Core–valence correlation					
Restricted minimal-reference configuration interaction					
s-d[a]	−1.04915	0.095	0.717	6.605	7.041
s-f[a]	−1.13954	−0.149	0.940	6.280	7.028
s-g[a]	−1.15972	−0.231	1.016	6.181	7.026
s-h[a]	−1.16733	−0.261	1.043	6.147	7.026
$l \geq 6$ functions[a]	−1.17374	−0.294	1.075	6.112	7.027
Truncated natural orbitals[a]	−1.17386	−0.295	1.078	6.109	7.024
Core correlation					
Restricted minimal-reference configuration interaction					
s-d[a]	−1.32465	−0.048	0.847	6.410	7.028
s-f[a]	−1.36790	−0.009	0.810	6.461	7.029
s-g[a]	−1.38571	0.004	0.798	6.482	7.032
s-h[a]	−1.39175	0.003	0.799	6.487	7.035
$l \geq 6$ functions[a]	−1.40058	−0.004	0.807	6.492	7.043
Truncated natural orbitals[a]	−1.40082	−0.003	0.807	6.493	7.044
Relativistic effects[a]	−6.78412	0.189	0.636	6.779	7.072

[a] The estimated contribution is added to the energy obtained in the previous step

ences in general: 0.003–0.037 and 0.001–0.015 eV, respectively. However, the contributions were exceptionally large in the $3d^6 4s\ ^6D$ excited state of Mn, which is the only state possessing six 3*d* electrons and they decreased the excitation energy by 0.093 and 0.033 eV.

The contributions from the *f*, *g* and *h* functions to the valence correlation are plotted on a log–log scale in Fig. 1, which depicts those contributions for the various states of the V atom as an example. The contributions lie roughly on a straight line; on the assumption of this linearity, we extrapolated the contribution from $l \geq 6$ functions. Inclusion of the contributions from $l \geq 6$ functions brought about a nonnegligible change (decrease of 0.025 eV) only to the excitation energy of Mn, but little changes to the other energy differences (0.006 eV at most). It should be noted that the contributions from higher *l* functions are more significant for states possessing more 3*d* electrons and are exceptionally large for $3d^6 4s\ ^6D$ of Mn.

Plots of the CI and CI + Q energies against the weight of the reference space, *w*, are depicted in Fig. 2 for V $3d^3 4s^2\ ^4F$, $3d^4 4s\ ^6D$ and V^- $3d^4 4s^2\ ^5D$ as examples. The valence–full CI limits were obtained by averaging the CI and CI + Q energies of the largest-scale CI instead of extrapolating the curves to $w = 1$, since *w* in the largest-scale CI wavefunction was far from 1 and further expansion of the reference space was impracticable because of computational limitation.

As shown in Fig. 2, both the CI and CI + Q energies with the minimal-reference space were far from the valence-full CI limit. It can be also seen that the CI and CI + Q energies converged much more slowly for the negative ion than for the neutral ground state. The use of the valence-full CI energies instead of the minimal-reference CI energies enlarged the EAs of V and Cr by about 0.1 eV.

In the valence CI calculations, errors due to the NO truncation were around 1.0×10^{-4} au for the total energies and less than 0.001 eV for the energy separations.

3.1.2 Core–valence and core correlation

The calculated core–valence correlation energies were −0.202 to −0.228, −0.249 to −0.271 and −0.267 to −0.307 au, and the core correlation energies were −0.213 to −0.227, −0.194 to −0.208 and −0.183 to −0.204 au for the various states of V, Cr and Mn,

Table 2. The excitation energies, EAs and IPs of the Cr atom (in eV). The total energies (+1043 au) are given for the ^7S state

Calculation	Total energy	Excitation energy	EA	IP	
	$3d^5 4s\ ^7S$	$3d^4 4s^2\ ^5D$	$3d^5 4s^2\ ^6S$	$3d^5\ ^6S$	$3d^4 4s\ ^6D$
Multiconfiguration self-consistent field	−0.40531	1.176	−0.055	6.019	7.725
Valence correlation					
Minimal-reference single and double excitation configuration interaction					
s-d	−0.41854	0.918	0.527	6.217	7.878
s-f	−0.46110	1.128	0.509	6.441	8.197
s-g	−0.46544	1.114	0.528	6.456	8.213
s-h	−0.46684	1.118	0.532	6.458	8.226
Full-configuration interaction limit	−0.46809	1.103	0.631	6.482	8.246
$l \geq 6$ functions[a]	−0.46869	1.103	0.634	6.481	8.251
Truncated natural orbitals[a]	−0.46876	1.103	0.635	6.481	8.250
Core–valence correlation					
Restricted minimal-reference configuration interaction					
s-d[a]	−0.57188	1.266	0.659	6.737	8.509
s-f[a]	−0.68694	1.432	0.649	6.682	8.666
s-g[a]	−0.71679	1.526	0.645	6.667	8.759
s-h[a]	−0.72799	1.560	0.644	6.660	8.790
$l \geq 6$ functions[a]	−0.73884	1.607	0.642	6.653	8.837
Truncated natural orbitals[a]	−0.73903	1.609	0.643	6.651	8.836
Core correlation					
Restricted minimal-reference configuration interaction					
s-d[a]	−0.86131	1.334	0.650	6.698	8.562
s-f[a]	−0.90139	1.293	0.651	6.708	8.524
s-g[a]	−0.91838	1.281	0.652	6.711	8.510
s-h[a]	−0.92469	1.282	0.652	6.710	8.512
$l \geq 6$ functions[a]	−0.93480	1.293	0.652	6.707	8.521
Truncated natural orbitals[a]	−0.93504	1.291	0.652	6.707	8.520
Relativistic effects[a]	−7.38568	1.055	0.718	6.813	8.309

[a] The same as in Table 1

respectively. There was a natural tendency for the magnitude of the core–valence correlation energy to increase with the atomic number. There also seemed to be a natural tendency for the magnitude of the core–valence correlation energy to increase with the number of $3d$ electrons in the respective atomic species. The magnitude of the core correlation energy exhibited the opposite tendency, decreasing with the atomic number and with the number of $3d$ electrons in the respective atomic species. This also seems to be natural, considering that an increase in the number of valence electrons reduces the orbital space to which two of the $3s^2 3p^6$ electrons are excited. A reduction in the d-orbital space is especially significant, since the excitations of $3p^2 \rightarrow nd^2$, $ndn'd$ and $3s3p \rightarrow npn'd$ are the most effective ones.

The contributions from the g and h functions to the core–valence correlation modified the energy separations between the two states possessing different numbers of $3d$ electrons by around 0.1 and 0.03 eV, respectively. The contributions from the g functions to the core correlation modified the energy separations by around 0.02 eV at most, and those from the h functions caused much smaller modifications.

When the contributions from $l \geq 6$ functions to the core–valence correlation were included, nonnegligible modifications of around 0.05 eV also occurred in the energy separations between the two states possessing different numbers of $3d$ electrons: the largest one was the increase of 0.066 eV in the IP of Mn for $3d^4 4s^2\ ^5D$. The modifications of the energy differences caused by the contributions from $l \geq 6$ functions to the core correlation were much smaller than those caused by the contributions from $l \geq 6$ functions to the core–valence correlation; the largest one also appeared in the IP of Mn, but was only 0.014 eV. It is clear that such calculations that include the core effects using only *s-f* functions produce an error of around 0.2 eV for several cases.

In the CV-CI and C-CI calculations, errors due to the NO truncation were $1.2 - 2.6 \times 10^{-4}$ and $1.8 - 3.6 \times 10^{-4}$ au, respectively, for the total energies and less than 0.003 and 0.002 eV for the energy differences.

3.1.3 Relativistic effects

The relativistic corrections to the energy separations, which were evaluated from the difference between the HF and Dirac–Fock energies for respective states, are given in Table 4. Large contributions are seen in the

Table 3. The excitation energies and IPs of the Mn atom (in eV). The total energies (+1149 au) are given for the ^6S state

Calculation	Total energy	Excitation energy	IP	
	$3d^5 4s^2\ ^6S$	$3d^6 4s\ ^6D$	$3d^5 4s\ ^7S$	$3d^4 4s^2\ ^5D$
Multiconfiguration self-consistent field	−0.93227	3.025	6.658	13.894
Valence correlation				
Minimal-reference single and double excitation configuration interaction				
s-d	−0.95765	2.758	7.095	14.108
s-f	−1.00871	2.459	7.216	14.441
s-g	−1.01498	2.366	7.253	14.460
s-h	−1.01693	2.333	7.262	14.475
Full configuration interaction limit	−1.01895	2.274	7.295	14.506
$l \geq 6$ functions[a]	−1.01989	2.249	7.301	14.511
Truncated natural orbitals[a]	−1.02000	2.249	7.302	14.511
Core–valence correlation				
Restricted minimal-reference configuration interaction				
s-d[a]	−1.12998	1.916	7.373	14.764
s-f[a]	−1.25230	1.923	7.368	14.925
s-g[a]	−1.28552	1.876	7.367	15.039
s-h[a]	−1.29806	1.860	7.366	15.080
$l \geq 6$ functions[a]	−1.31081	1.824	7.365	15.146
Truncated natural orbitals[a]	−1.31104	1.825	7.366	15.148
Core correlation				
Restricted minimal-reference configuration interaction				
s-d[a]	−1.42327	1.896	7.368	14.742
s-f[a]	−1.46318	1.928	7.370	14.685
s-g[a]	−1.48034	1.940	7.370	14.667
s-h[a]	−1.48684	1.941	7.370	14.667
$l \geq 6$ functions[a]	−1.49778	1.938	7.369	14.681
Truncated natural orbitals[a]	−1.49808	1.936	7.369	14.681
Relativistic effects[a]	−9.18910	2.095	7.395	14.296

[a] The same as in Table 1

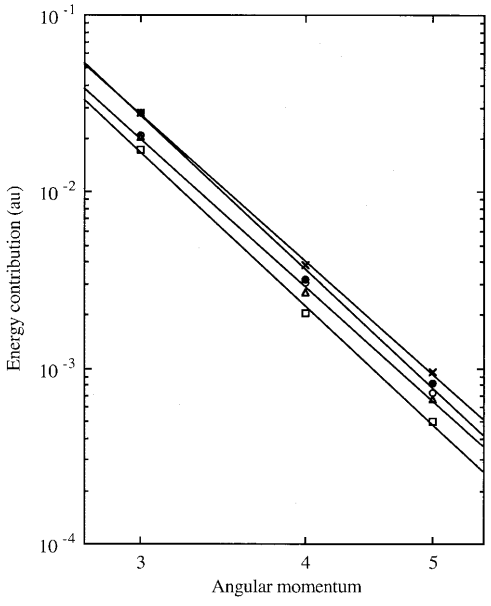

Fig. 1. Contributions from the respective l functions to the valence correlation energies: V $3d^3 4s^2\ ^4F$ (○); V $3d^4 4s\ ^6D$ (●); $V^- 3d^4 4s^2\ ^5D$ (×); $V^+ 3d^4\ ^5D$ (△); $V^+ 3d^3 4s\ ^5F$ (□). The absolute values of the contributions are plotted on a log–log scale

transitions with a change of the occupation of the 3*d* subshell. The relativistic effects destabilize the states generated by the transition with an increase in the number of 3*d* electrons, while they stabilize those generated by the transition with a decrease.

Martin and Hay [32] studied relativistic contributions to the low-lying excitation energies and IPs of transition-metal atoms. Their relativistic operator is not a fully relativistic Dirac–Fock operator but includes the mass-velocity and Darwin terms of the one-electron Pauli equation in addition to the nonrelativistic HF operator. As shown in Table 4, however, their results closely resemble our own.

3.2 Excitation energies, EAs and IPs

The calculated excitation energies, EAs and IPs are compared with previous theoretical and experimental values in Tables 5, 6 and 7.

3.2.1 Excitation energy

We calculated the $3d^n 4s^2 \rightarrow 3d^{n+1} 4s$ excitation energy for the V and Mn atoms, but the $3d^{n+1} 4s \rightarrow 3d^n 4s^2$ excitation energy for the Cr atom. By considering only valence correlation, the excitation energies were calcu-

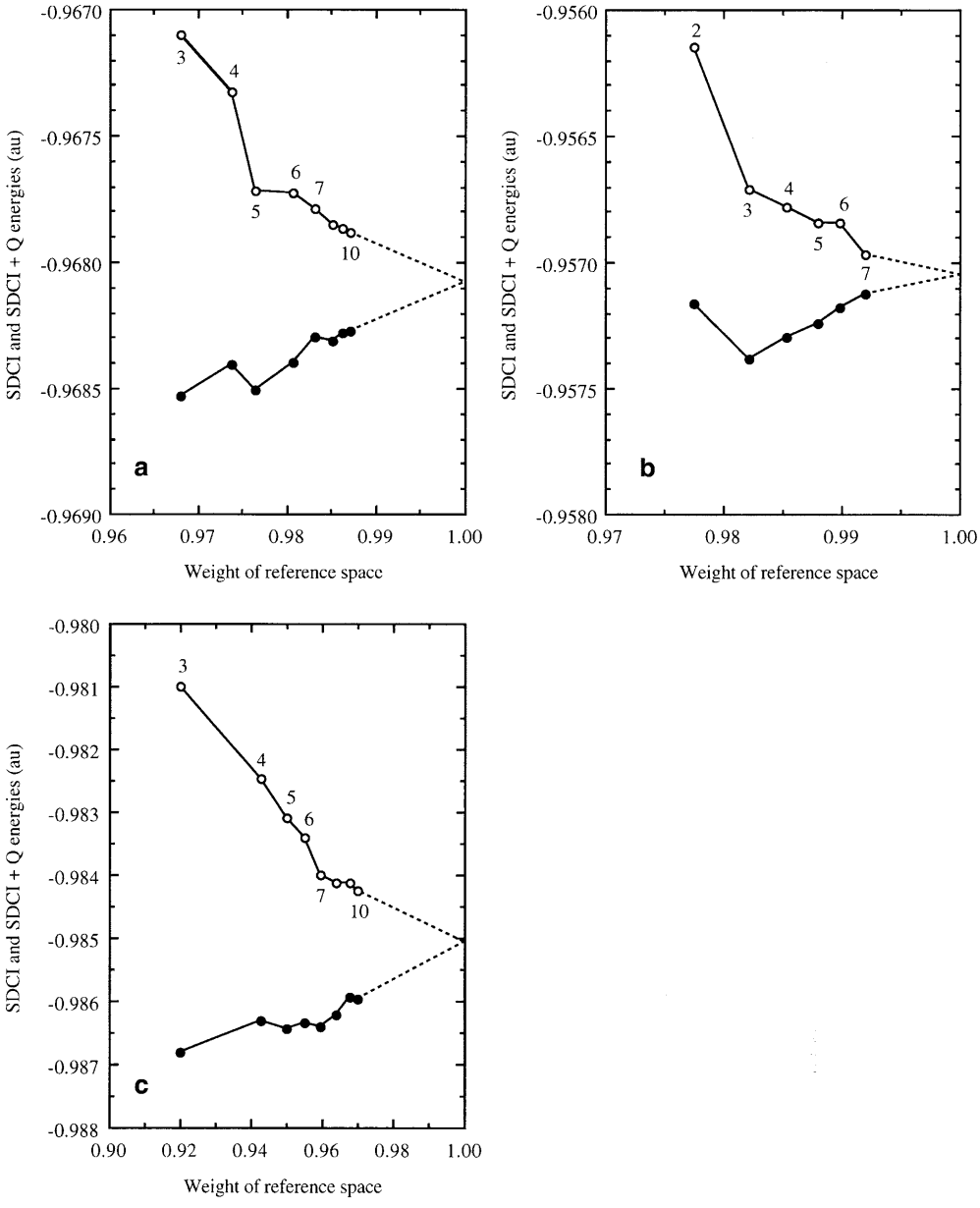

Fig. 2. Multireference single and double excitation configuration interaction (MRSDCI) and the multireference analogue of Davidson's correction (MRSDCI + Q) energies as a function of the weight of the reference space for **a** V $3d^3 4s^2\ ^4F$, **b** V $3d^4 4s\ ^6D$ and **c** V^- $3d^4 4s^2\ ^5D$: MRSDCI (○); MRSDCI + Q (●). The *digits* in the figures indicate the number of reference configurations

lated to be 0.301, 1.103 and 2.249 eV for V, Cr and Mn, respectively. Inclusion of the core–valence correlation decreased the excitation energies of V and Mn by 0.596 and 0.424 eV, respectively, while it increased that of Cr by 0.506 eV. These effects of the core–valence correlation are reasonable, since the excitations of V and Mn are accompanied by an increase in the number of 3*d* electrons, while that of Cr is accompanied by a decrease. Inclusion of the core correlation increased the excitation energies of V and Mn by 0.292 and 0.111 eV, respectively, while it decreased that of Cr by 0.318 eV. Thus the nonrelativistic excitation energies were calculated as −0.003, 1.291 and 1.936 eV for V, Cr and Mn, respectively. Finally, by including the relativistic corrections, we obtained excitation energies of 0.189, 1.055 and 2.095 eV for V, Cr and Mn; the values were in good agreement with the respective observed values (deviation 0.056 eV or less).

In previous variational calculations [6, 7], the (14*s*, 9*p*, 5*d*) primitive Gaussian basis set of Wachters [35] was used and augmented with a few additional *s-f* functions. Botch et al. [6] obtained excitation energies of 0.40, 1.10 and 3.07 eV by multiconfiguration self-consistent-field (MCSCF) calculations for V, Cr and Mn, respectively; the values were 0.07 eV larger, 0.08 eV smaller and 0.04 eV larger than our MCSCF values. These discrepancies indicate a deficiency of their *d* basis functions; they contracted the six *d* primitives to three, while eight or nine *d* STFs were actually needed in the present calculations. They also performed valence SDCI calculations using only a single *f* function and reported excitation energies of 0.41 and 1.04 eV for V and Cr, respectively, with MCSCF reference functions, which is what we call minimal-reference space; these values were 0.11 eV larger and 0.06 eV smaller than our valence CI results. By comparing these results with our present

results of minimal-reference valence CI with an *s-f* set, it can be concluded that the valence correlation cannot be described properly by a single *f* function.

Bauschlicher et al. [7] performed single-reference SDCI calculations including the excitations of the 3*s* and 3*p* electrons and reported nonrelativistic excitation energies of 0.27, 1.04 and 2.64 eV for V, Cr and Mn, respectively, with Davidson's correction. These values differ from ours by 0.25–0.70 eV. These discrepancies can be attributed to both the deficiency of their basis set and their single-reference treatment. Just as for Botch et al., their *d* and *f* functions are insufficient. The core–valence correlation cannot be described properly without *g* and the higher *l* functions, as discussed previously. For the excitation energy of Mn, where the largest deviation from our results appears, contributions from *g* and *h* functions to the valence correlation are also important; those contributions are 0.093 and 0.033 eV larger in $3d^6 4s\ ^6D$ than in $3d^5 4s^2\ ^6S$. Inclusion of the excitations of the 3*s* and 3*p* electrons in a single-reference SDCI deteriorates the description of the valence correlation because of the lack of size consistency in the CI method, and both the CI and CI + Q energies are probably far from the full CI energy.

Raghavachari and Trucks [19] obtained excitation energies comparable to those of Bauschlicher et al. by the quadratic CI (QCI) method, considering the correlation of 3*s*, 3*p*, 3*d* and 4*s* electrons. The basis set employed, a [10*s*, 7*p*, 4*d*, 3*f*] contracted Gaussian basis set composed of a (15*s*, 11*p*, 6*d*, 3*f*) primitive set, was similar to that of Bauschlicher et al. This is considered to be responsible for the deviations from the present results.

Table 4. The relativistic corrections (in eV) to excitation energies, EAs and IPs. A value with a *plus* sign indicates that the state is destabilized with respect to the neutral ground state and that with a *minus* sign indicates that the state is stabilized

Atom	State	Present	MH[a]
V	$3d^3 4s^2\ ^4F$	0.000	0.00
V	$3d^4 4s\ ^6D$	+0.192	+0.14
V^-	$3d^4 4s^2\ ^5D$	+0.171	
V^+	$3d^4\ ^5D$	+0.286	+0.25
V^+	$3d^3 4s\ ^5F$	+0.028	+0.03
Cr	$3d^5 4s\ ^7S$	0.000	0.00
Cr	$3d^4 4s^2\ ^5D$	−0.236	−0.17
Cr^-	$3d^5 4s^2\ ^6S$	−0.066	
Cr^+	$3d^5\ ^6S$	+0.106	+0.09
Cr^+	$3d^4 4s\ ^6D$	−0.211	−0.17
Mn	$3d^5 4s^2\ ^6S$	0.000	0.00
Mn	$3d^6 4s\ ^6D$	+0.159	+0.17
Mn^+	$3d^5 4s\ ^7S$	+0.026	+0.05
Mn^+	$3d^4 4s^2\ ^5D$	−0.385	

[a] Ref. [32]

3.2.2 Electron affinity

The EAs calculated considering only the valence correlation were 0.466 and 0.635 eV for V and Cr, respectively. Inclusion of the core–valence correlation

Table 5. Comparison of the calculated excitation energies, EAs and IPs (in eV) with the previous theoretical and experimental results for the V atom

Method	Excitation energy	EA	IP	
	$3d^4 4s\ ^6D$	$3d^4 4s^2\ ^5D$	$3d^4\ ^5D$	$3d^3 4s\ ^5F$
Present				
MCSCF	0.330	−0.275	6.127	6.430
Valence correlation	0.301	0.466	6.528	6.930
+ core–valence correlation	−0.295	1.078	6.109	7.024
+ core correlation	−0.003	0.807	6.493	7.044
+ relativistic corrections	0.189	0.636	6.779	7.072
Previous theoretical calculations[a]				
MCSCF[b]	0.40			
SDCI (HF)[b]	0.38			
SDCI (MCSCF)[b]	0.41			
SDCI[c]	0.36			
SDCI + Q[c]	0.46			
SDCI (3*s*3*p*)[c]	0.12			
SDCI (3*s*3*p*) + Q[c]	0.27			
QDMBPT[d]	0.006	−0.49	6.51	6.943
QDMBPT[e]	0.406			6.811
QCISD (T)	0.21[f]		6.59[g]	6.94[g]
Observed	0.245[h]	0.526[i]	6.726[h]	7.063[h]

[a] All the previous calculations are nonrelativistic, and relativistic corrections should be considered when comparisons with the observed values are made
[b] Ref. [6]
[c] Ref. [7]
[d] Ref. [8]; with orbitals and orbital energies from $^5F(d^3 s^1)$
[e] Ref. [8]; with orbitals and orbital energies from the average of $^5F(d^3 s^1)$ and $^6D(d^4 s^1)$
[f] Ref. [19]
[g] Ref. [20]
[h] Ref. [33]
[i] Ref. [34]

Table 6. Comparison of the calculated excitation energies, EAs and IPs (in eV) with the previous theoretical and experimental results for the Cr atom

Method	Excitation energy	EA	IP	
	$3d^4 4s^2\ ^5D$	$3d^5 4s^2\ ^6S$	$3d^5\ ^6S$	$3d^4 4s\ ^6D$
Present				
MCSCF	1.176	−0.055	6.019	7.725
Valence correlation	1.103	0.635	6.481	8.250
+ core–valence correlation	1.609	0.643	6.651	8.836
+ core correlation	1.291	0.652	6.707	8.520
+ relativistic corrections	1.055	0.718	6.813	8.309
Previous theoretical calculations[a]				
MCSCF[b]	1.10			
SDCI (HF)[b]	1.09			
SDCI (MCSCF)[b]	1.04			
SDCI[b]	1.09			
SDCI + Q[c]	0.95			
SDCI ($3s3p$)[c]	1.20			
SDCI ($3s3p$) + Q[c]	1.04			
QDMBPT[d]	1.817			9.496
QDMBPT[e]	1.554	0.40	6.54	8.631
QDMBPT[f]	0.636			7.678
QCISD (T)	1.10[g]		6.64[h]	8.23[h]
GMP2[i]	1.04			
GMP2 ($3s3p$)[i]	1.10			
Observed	1.003[j]	0.667[k]	6.767[j]	8.287[j]

[a] The same as in Table 5
[b] Ref. [6]
[c] Ref. [7]
[d] Ref. [8]; with orbitals and orbital energies from $^5F\ (d^3s^1)$
[e] Ref. [8]; with orbitals and orbital energies from $^5D(d^4s^2)$
[f] Ref. [8]; with orbitals and orbital energies from the average of $^7S(d^5s^1)$ and $^5D(d^4s^2)$
[g] Ref. [19]
[h] Ref. [20]
[i] Ref. [22]
[j] Ref. [33]
[k] Ref. [34]

increased the EAs of V and Cr by 0.612 and 0.008 eV, respectively. This large difference of the core–valence correlation effects is considered to be reasonable, since an extra electron occupies the $3d$ subshell in V^-, but the $4s$ subshell in Cr^-. Inclusion of the core correlation decreased the EA of V by 0.271 eV, while it increased that of Cr by 0.009 eV. By including the relativistic correction, we obtained EAs of 0.636 and 0.718 eV for V and Cr, respectively, which are 0.110 and 0.051 eV larger than the observed values. Lee and Freed [8] reported EAs of −0.49 and 0.40 eV for V and Cr, respectively, by applying quasidegenerate many-body perturbation theory, which is the only previous theoretical study of the EAs of these atoms.

3.2.3 Ionization potentials

The lowest ionized state of the first transition-metal atoms is usually generated by the ionization of the $4s$ electron. For the V atom, however, the lowest ionized state is known to be $3d^4\ ^5D$, and thus the lowest ionization of V is exceptionally accompanied by an increase in the number of $3d$ electrons. At the valence CI level, the lowest IP of V was calculated to be 6.528 eV. The core–valence correlation decreased this value by 0.419 eV and the core correlation increased it by 0.384 eV. Inclusion of the relativistic effects increased the IP by 0.286 eV, resulting in a value of 6.779 eV, which is only 0.053 eV larger than the experimental value.

In the ionizations of the $4s$ electron, the effects of both the core–valence and the core correlation are rather small but significant for all three atoms; the largest modifications due to the core–valence and core correlation effects appeared in the IP of Cr and were increases of 0.170 and 0.056 eV, respectively. The relativistic effects also brought about small changes in these IPs. The calculated IPs were 7.072, 6.813 and 7.395 eV for V, Cr and Mn, respectively; the values were in excellent agreement with the observed values (deviation 0.046 eV or less).

In the ionizations of the $3d$ electron, on the other hand, the effects of the core–valence and core correlation were fairly large; the core–valence correlation increased the IPs of Cr and Mn by 0.586 and 0.637 eV, respectively, and the core correlation decreased them by 0.316 and 0.467 eV. The relativistic effects decreased the IPs of Cr and Mn by 0.211 and 0.385 eV to 8.309 and 14.296 eV, respectively; these values were also in excellent agreement with the observed values (deviation 0.022 eV or less).

The nonrelativistic IPs given by the QCI method [20] differ from ours by 0.07–0.29 eV. As discussed previ-

Table 7. Comparison of the calculated excitation energies and IPs (in eV) with the previous theoretical and experimental results for the Mn atom

Method	Excitation energy	IP	
	$3d^6 4s\ ^6D$	$3d^5 4s\ ^7S$	$3d^4 4s^2\ ^5D$
Present			
MCSCF	3.025	6.658	13.894
Valence correlation	2.249	7.302	14.511
+ core–valence correlation	1.825	7.366	15.148
+ core correlation	1.936	7.369	14.681
+ relativistic corrections	2.095	7.395	14.296
Previous theoretical calculations[a]			
MCSCF[b]	3.07		
SDCI[c]	2.77		
SDCI + Q[c]	2.86		
SDCI ($3s3p$)[c]	2.64		
SDCI ($3s3p$) + Q[d]	2.64		
QCISD (T)	2.24[d]	7.28[e]	
Observed[f]	2.145	7.432	14.296

[a] The same as in Table 1
[b] Ref. [6]
[c] Ref. [7]
[d] Ref. [19]
[e] Ref. [20]
[f] Ref. [33]

ously (Sect. 3.2.1), these discrepancies were attributed to a deficiency of the basis set in the former study. The contributions from the g, h and $l \geq 6$ functions to the core–valence correlation were especially significant. For example, those in Cr $3d^5 4s\ ^7S$ were 0.093, 0.031 and 0.047 eV larger than those in Cr^+ $3d^4 4s\ ^6D$, and the sum of these deviations was comparable to the deviation from ours in the IP of the $3d$ electron of Cr, 0.29 eV.

4 Summary

Systematic CI calculations were performed on the V, Cr and Mn atoms and their ions. Energy convergence with respect to both the one-electron and configuration bases were investigated at the valence CI level. The core–valence and core correlation energies and the relativistic effects were estimated separately. Assuming the additivity of these contributions, the excitation energies, EAs and IPs were calculated in excellent agreement with the observed values (deviation 0.056 eV or less) except for the EA of the V atom, which had a calculated value 0.110 eV larger than the observed value. In order to obtain more reliable results, coupling among the valence, core–valence and core correlations and the relativistic effects must be considered. The values reported here should be useful reference points for future molecular calculations.

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