

## Paircorrelation energy and successive ionization potentials of atoms He–Zn

M. Vijayakumar and M. S. Gopinathan

Citation: *The Journal of Chemical Physics* **97**, 6639 (1992); doi: 10.1063/1.463667

View online: <http://dx.doi.org/10.1063/1.463667>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/97/9?ver=pdfcov>

Published by the [AIP Publishing](#)

---

### Articles you may be interested in

[Fluctuation of the pair-correlation function](#)

*J. Chem. Phys.* **107**, 8575 (1997); 10.1063/1.475009

[Chemical potential, ionization energies, and electron correlation in atoms](#)

*J. Chem. Phys.* **76**, 1869 (1982); 10.1063/1.443159

[Excitation mechanisms in He–Cd and He–Zn ion lasers](#)

*J. Appl. Phys.* **44**, 4633 (1973); 10.1063/1.1662014

[On the QuantumMechanical PairCorrelation Function of 4He Gas at Low Temperatures](#)

*J. Chem. Phys.* **44**, 213 (1966); 10.1063/1.1726449

[Spin Properties of PairCorrelated Atomic and Molecular Singlet Wavefunctions](#)

*J. Chem. Phys.* **40**, 595 (1964); 10.1063/1.1725164

---



# Pair-correlation energy and successive ionization potentials of atoms He–Zn

M. Vijayakumar and M. S. Gopinathan

*Department of Chemistry, Indian Institute of Technology, Madras 600 036, India*

(Received 23 May 1991; accepted 15 June 1992)

The successive ionization potentials (IP's) of atoms He–Zn are calculated using the relativistic and correlated local-density RCE method. The contribution of correlation energy to IP's of these atoms are reported. It is found that these correlation contribution to IP's are different for different IP's of the same atom. It is also different for a given IP for different atoms. This behavior is qualitatively explained on the basis of the results of pair-correlation energy. A simple approximate expression to calculate the pair-correlation energy proposed earlier is discussed.

## I. INTRODUCTION

It has been reported in literature that the first ionization potentials<sup>1–5</sup> and electron affinities<sup>1–6</sup> of atoms are considerably improved due to correlation. We have also reported<sup>7</sup> the effect of correlation on valence orbital ionization energies and electron affinities of atoms. Many authors<sup>4–7</sup> also pointed out that for the accurate calculation and for predicting the stability of negative ions, correlation has to be incorporated in the theoretical calculations.

We have recently reported a fully correlated relativistic method called relativistic and correlated  $\Xi$  method, or briefly, the RCE method.<sup>7</sup> In the RCE method, the correlation has been explicitly incorporated. It has been shown that the RCE method recovers about 80–100 % correlation with respect to exact correlation energy for atoms He–Ar. The correlation energy for all the atoms in the periodic table have been calculated<sup>7</sup> by us.

We have applied the RCE method to calculate the successive ionization potentials (IP's) for atoms He–Zn. We report the results in this paper. The contribution of the correlation energy to the ionization potentials have been computed presently. It is found that for the given atom, the correlation contributions to IP's are different for different ionization potentials, i.e., the contribution of correlation energy to first (I), second (II), and third (III) IP's are different for the same atom. For the given IP, the contribution of correlation energy is different for different atoms, i.e., for the first ionization potential, say for example, it is different for different atoms. Using the pair-correlation energy, the correlation contribution to the IP's have been qualitatively explained. Although the contributions are of the order of 0.2–1.0 eV, an attempt has been made in this paper to explain them in a qualitative manner.

In Sec. II the method of calculation of pair-correlation energy is briefly described and the results are discussed. Using the resulting pair-correlation energy, the correlation contribution to the IP's are explained in Sec. III.

## II. METHOD OF CALCULATION OF PAIR-CORRELATION ENERGY

In this section, the method of calculation of pair-correlation energy and the results are discussed. Using the

following expression, the correlation energy of the system in the RCE method<sup>7</sup> has been calculated:

$$E^{\text{corr}} = \frac{1}{2} \int \rho_{\uparrow}(r) V_{\uparrow}^{\text{corr}}(r) dr + \frac{1}{2} \int \rho_{\downarrow}(r) V_{\downarrow}^{\text{corr}}(r) dr, \quad (1)$$

where  $\rho_{\uparrow}(r)$  and  $\rho_{\downarrow}(r)$  denote the up-spin and down-spin electron densities, respectively, and  $V_{\uparrow}^{\text{corr}}(r)$  is the Coulomb correlation potential acting upon an up-spin electron due to the potential being produced by all the down-spin electrons which is given as

$$V_{\uparrow}^{\text{corr}}(r) = -\frac{8}{27} X^3 \left[ \pi \left( \frac{1}{n_{\uparrow}} + \frac{1}{3} \right) \rho_{\downarrow}(r) \right]^{-1} \left\{ X \left[ \pi \left( \frac{1}{n_{\downarrow}} + \frac{1}{3} \right) \rho_{\downarrow}(r) \right]^{-1/3} + 1 \right\}^{-1} \rho_{\downarrow}(r), \quad (2)$$

where  $X$  is the parameter with the value 0.75 and  $n$  is the number of down-spin electrons in the system, and a similar expression for  $V_{\downarrow}^{\text{corr}}(r)$ . It is to be mentioned that  $V_{\uparrow}^{\text{corr}}(r)$  is derived using the two important properties of Coulomb hole namely the cusp condition on the wave function and charge conservation.<sup>8,9</sup>

The correlation energy discussed earlier can be partitioned into pairwise contributions. The average pair-correlation energy for any pair ( $i, j$ ) is defined as (see Ref. 10 for the detailed calculation of pair-correlation energy)

$$e(i, j) = \frac{\langle e(i_{\uparrow}, j_{\downarrow}) \rangle + \langle e(i_{\downarrow}, j_{\uparrow}) \rangle}{2}, \quad (3)$$

where  $\langle e(i, j) \rangle$  is given as

$$\langle e(i, j) \rangle = \frac{e(i_{\uparrow}, j_{\downarrow}) + e(j_{\downarrow}, i_{\uparrow})}{2} \quad (4)$$

and a similar expression for  $\langle e(i_{\downarrow}, j_{\uparrow}) \rangle$ . The term in Eq. (4)  $e(i_{\uparrow}, j_{\downarrow})$  is defined as the correlation energy between an up-spin electron in  $u_{i_{\uparrow}}$  and a down-spin electron in  $u_{j_{\downarrow}}$  and is given as

$$e(i_{\uparrow}, j_{\downarrow}) = \int [V_{\uparrow}^{\text{corr}}(r)]_{i_{\uparrow}} u_{j_{\downarrow}}^*(r) u_{j_{\downarrow}}(r) dr, \quad (5)$$

and a similar expression for  $e(j_{\downarrow}, i_{\uparrow})$ . The term  $[V_{\uparrow}^{\text{corr}}(r)]_{i_{\uparrow}}$  in Eq. (5) is defined as the correlation potential produced

TABLE I. Pair-correlation energy (in Ry) for Ar.

Pair <sup>a</sup>	Pair-correlation energy <sup>b</sup>
(1s <sub>+</sub> ,1s <sub>+</sub> )	-0.1849
(1s <sub>+</sub> ,2s <sub>+</sub> )	-0.0108
(1s <sub>+</sub> ,2p <sub>-</sub> )	-0.0156
(1s <sub>+</sub> ,2p <sub>+</sub> )	-0.0153
(1s <sub>+</sub> ,3s <sub>+</sub> )	-0.0012
(1s <sub>+</sub> ,3p <sub>-</sub> )	-0.0013
(1s <sub>+</sub> ,3p <sub>+</sub> )	-0.0012
(2s <sub>+</sub> ,2s <sub>+</sub> )	-0.0460
(2s <sub>+</sub> ,2p <sub>-</sub> )	-0.0416
(2s <sub>+</sub> ,2p <sub>+</sub> )	-0.0417
(2s <sub>+</sub> ,3s <sub>+</sub> )	-0.0044
(2s <sub>+</sub> ,3p <sub>-</sub> )	-0.0030
(2s <sub>+</sub> ,3p <sub>+</sub> )	-0.0030
(2p <sub>-</sub> ,2p <sub>-</sub> )	-0.0434
(2p <sub>-</sub> ,2p <sub>+</sub> )	-0.0433
(2p <sub>-</sub> ,3s <sub>+</sub> )	-0.0042
(2p <sub>-</sub> ,3p <sub>-</sub> )	-0.0032
(2p <sub>-</sub> ,3p <sub>+</sub> )	-0.0031
(2p <sub>+</sub> ,2p <sub>+</sub> )	-0.0432
(2p <sub>+</sub> ,3s <sub>+</sub> )	-0.0042
(2p <sub>+</sub> ,3p <sub>-</sub> )	-0.0032
(2p <sub>+</sub> ,3p <sub>+</sub> )	-0.0031
(3s <sub>+</sub> ,3s <sub>+</sub> )	-0.0274
(3s <sub>+</sub> ,3p <sub>-</sub> )	-0.0243
(3s <sub>+</sub> ,3p <sub>+</sub> )	-0.0242
(3p <sub>-</sub> ,3p <sub>-</sub> )	-0.0233
(3p <sub>-</sub> ,3p <sub>+</sub> )	-0.0233
(3p <sub>+</sub> ,3p <sub>+</sub> )	-0.0233

<sup>a</sup>Note that the symbol (+) means  $j=1+\frac{1}{2}$  and the symbol (-) means  $j=1-\frac{1}{2}$ .

<sup>b</sup>The pair-correlation energy is calculated by the present method using the expression given in Eq. (3) of the text.

by an up-spin electron in the  $i$ th spin orbital experienced by a down-spin electron and is given by

$$[V_i^{\text{corr}}(r)]_i = \frac{V_i^{\text{corr}}(r)u_i^*(r)u_i(r)}{\rho_i(r)} \quad (6)$$

and a similar expression for  $[V_i^{\text{corr}}(r)]_j$ ;  $V_i^{\text{corr}}(r)$  is the correlation potential felt by a down-spin electron as produced by all the up-spin electrons.

Using Eq. (3), the pair-correlation energies for various atoms have been calculated earlier, and compared with the pair-correlation energies calculated by other methods.<sup>10</sup> In this section, we now discuss the pair-correlation energies calculated by the present method and we use these results in the next section to discuss ionization potentials.

In Table I, the pair-correlation energies, for instance for the argon atom, calculated by the present method are shown. It is seen that the intershell correlation energy is less than the intrashell correlation energy. For example, the correlation energy for the pair (1s<sub>+</sub>,1s<sub>+</sub>) is large compared to that of (1s<sub>+</sub>,2s<sub>+</sub>) and for the pair (2s<sub>+</sub>,2s<sub>+</sub>), it is larger than that for the pair (2s<sub>+</sub>,3s<sub>+</sub>), and so on. Within the shell, the pair-correlation energy for inner orbital is slightly larger than that for the outer orbitals of the same shell; for example, the pair-correlation energy of the pair

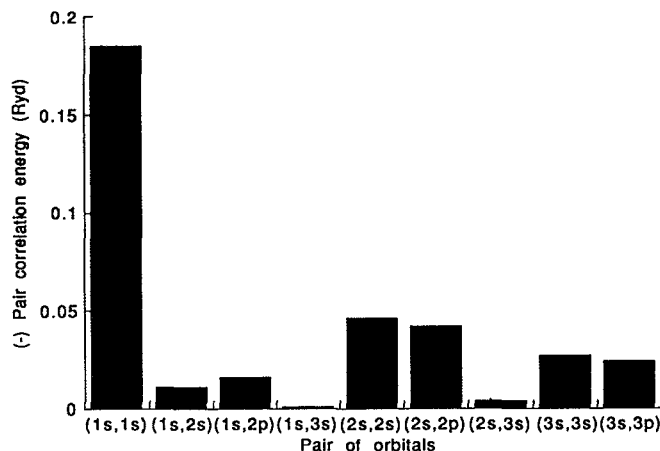


FIG. 1. Plot of intershell and intrashell pair-correlation energies of argon.

(2s<sub>+</sub>,2s<sub>+</sub>) is slightly larger than that for the pairs (2s<sub>+</sub>,2p<sub>-</sub>), (2s<sub>+</sub>,2p<sub>+</sub>), (2p<sub>-</sub>,2p<sub>-</sub>), and so on. The results are shown in Fig. 1.

### III. SUCCESSIVE IONIZATION POTENTIALS

In Table II, the I, II, and III IP's calculated by the present method without correlation (in columns 2, 6, and 10) and with the correlation (in columns 4, 8, and 10) are presented along with the experimental results<sup>11</sup> (in columns 5, 9, and 13).

In the RCE method the coupling scheme employed is the  $jj$ -coupling method. It is known that for the light atoms, the LS (Russell-Saunders) coupling is a favorable one. We carried the  $jj$ -LS transformation to get the total energies of elements and its ions which is presently done by separately calculating the energy for all the possible electronic configuration under the  $jj$ -coupling scheme. Then the weighted average of the total energy of these microstates is used for further calculations, i.e., for calculating the ionization potentials and the correlation contribution to ionization.

Using the  $\Delta$ SCF (self-consistent-field) procedure, the successive ionization potentials are calculated, i.e., the first IP is computed as the difference between the total energies of the neutral atom and its singly positive ion, the second IP as the difference between the total energies of the singly positive ion and its doubly positive ion and so on. The contribution of the correlation energy to these I, II, and III IP's are also given in columns 3, 7, and 11, respectively, in Table II, and are denoted by  $\Delta E_I$ ,  $\Delta E_{II}$ , and  $\Delta E_{III}$ , respectively. The correlation contribution, say the  $\Delta E_I$ , is calculated as the difference between the total correlation energy of the atom and its singly positive ion;  $\Delta E_{II}$  is the difference between the total correlation energies of the singly positive ion and its doubly positive ion, and so on.

In Fig. 2, the I, II, and III IP's calculated by the present method with correlation are plotted against the corresponding atomic numbers. As expected, all the IP's (i.e., I, II, and III) increase with the atomic number along the period and for a given atom, the IP's are in the ex-

TABLE II. Comparison of ionization potentials (eV) of atoms (He-Zn) with and without correlation.

Atom	First IP				Second IP				Third IP			
	No corr <sup>a</sup>	$\Delta E_I^b$	With <sup>c</sup> corr	Expt. <sup>d</sup>	No corr	$\Delta E_{II}$	With corr	Expt.	No corr	$\Delta E_{III}$	With corr	Expt.
He	24.01	0.55	24.56	24.59								
Li	4.40	0.35	4.75	5.39	74.89	0.63	75.52	75.64				
Be	8.50	0.55	9.05	9.32	17.64	0.40	18.04	18.21	152.6	0.94	153.6	153.9
B	7.77	0.50	8.27	8.29	23.52	0.65	24.17	25.15	37.97	0.46	38.44	37.92
C	9.30	0.77	10.07	11.26	23.94	0.62	24.56	24.38	45.85	0.95	46.80	47.86
N	12.36	0.69	13.07	14.54	27.28	0.92	28.19	29.61	47.04	0.71	47.75	47.43
O	14.51	0.65	15.16	13.61	32.58	0.83	33.41	35.15	52.18	1.04	53.22	54.93
F	17.09	1.17	18.27	17.41	36.60	0.77	37.47	34.98	59.77	0.93	60.69	62.65
Ne	19.58	1.07	20.66	21.55	41.14	1.33	42.47	41.07	65.63	0.86	66.49	64.00
Na	4.92	0.31	5.23	5.14	46.44	0.70	47.14	47.29	70.90	1.20	72.10	71.65
Mg	6.75	0.87	7.62	7.64	14.66	0.39	15.05	15.03	78.17	1.32	79.49	80.12
Al	5.51	0.57	6.08	5.98	17.59	0.82	18.41	18.82	28.17	0.65	28.82	28.44
Si	6.71	0.77	7.48	8.15	15.95	0.70	16.65	16.34	32.05	0.80	32.85	33.46
P	9.06	0.72	9.78	10.58	17.82	0.89	18.71	19.65	29.60	0.80	30.39	30.16
S	10.62	0.69	11.31	10.36	20.91	0.83	21.74	23.40	33.05	1.00	34.03	35.00
Cl	12.52	1.03	13.55	13.01	23.78	0.79	24.58	23.80	38.05	0.93	38.98	39.90
Ar	14.79	0.97	15.76	15.76	26.66	1.14	27.80	27.62	41.29	0.88	42.17	40.19
K	3.79	0.46	4.25	4.34	30.50	1.10	31.60	31.81	44.70	1.11	45.81	46.00
Ca	4.48	0.67	5.15	6.11	11.21	0.46	11.68	11.87	49.57	1.18	50.74	51.21
Sc	5.33	0.26	5.59	6.56	12.16	0.74	12.90	12.80	24.94	0.90	25.83	24.75
Ti	5.90	0.55	6.46	6.83	12.64	0.50	13.14	13.57	25.55	1.12	26.66	27.47
V	5.05	1.01	6.06	6.74	13.57	0.42	13.99	14.65	26.07	1.21	27.28	29.31
Cr	5.06	0.44	6.04	6.76	13.28	1.05	14.33	16.49	28.33	1.02	29.34	30.95
Mn	6.38	0.77	7.15	7.43	12.43	0.51	12.94	15.64	30.22	1.24	31.45	33.69
Fe	5.39	0.40	5.79	7.90	16.02	0.90	16.91	16.18	21.65	1.06	32.71	30.64
Co	6.60	0.87	7.48	7.86	15.21	0.49	15.70	17.05	34.21	1.03	35.24	33.29
Ni	7.28	0.84	8.12	7.63	15.41	0.54	15.95	18.15	35.28	1.34	36.62	35.16
Cu	7.32	0.54	7.86	7.72	16.95	1.11	18.06	20.29	36.81	1.29	38.11	36.83
Zn	7.62	0.79	8.41	9.39	14.86	0.63	15.49	17.96	37.97	1.25	39.23	39.70

<sup>a</sup>Ionization potential without correlation.

<sup>b</sup>Correlation contribution to ionization potential.

<sup>c</sup>Ionization potential with correlation.

<sup>d</sup>Experimental ionization potential values taken from Ref. 11.

pected order  $I < II < III$ . It is evident from Table II that the IP's calculated by the present with the correlation are in general closer to the experimental results than those without the correlation. It shows that the correlation is not only important to first ionization potentials but also to successive ionization potentials as well.

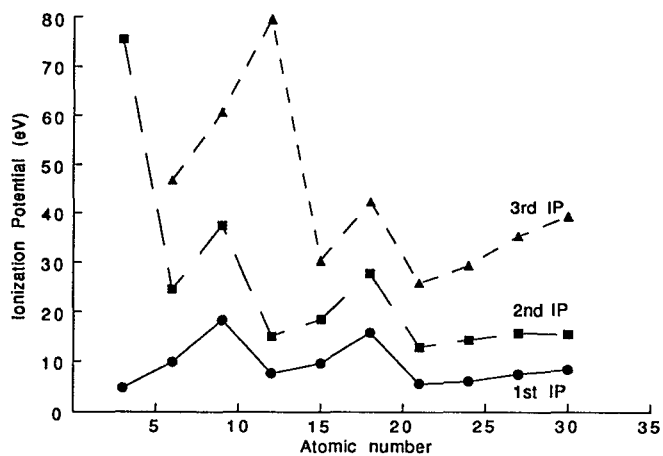


FIG. 2. Plot of I, II, and III ionization potentials vs atomic number.

We now discuss the contribution of the correlation energy to successive IP's. It may be seen from Table II and Figs. 3–6 that the correlation contribution to IP's is irregular and does not follow any pattern. However, it is found that these numbers could be qualitatively explained on the basis of the pair-correlation-energy results discussed in Sec. II. From our studies in Sec. II, it is found that the pair-correlation energy of electrons in the same shell is higher than the pair-correlation energy between electrons in different shells.

We now compare the contribution of the correlation energy to first ionization potential of first row elements calculated by different methods such as the gradient-corrected method proposed by Perdew<sup>12</sup> denoted by GCP, and with the "exact" results denoted by Exp which are calculated as the difference between the sum of the experimental ionization energies and the DHF total energy with quantum electrodynamic corrections. The GCP values which are obtained from the correlation energies of the atoms and its ions using the GCP method and the Exp values are taken from Ref. 5. The results are shown in Fig. 3. From Fig. 3 it is seen that the contribution of the correlation energy to first IP of Be is more than that of Li, in which there is only one electron present in the outer shell

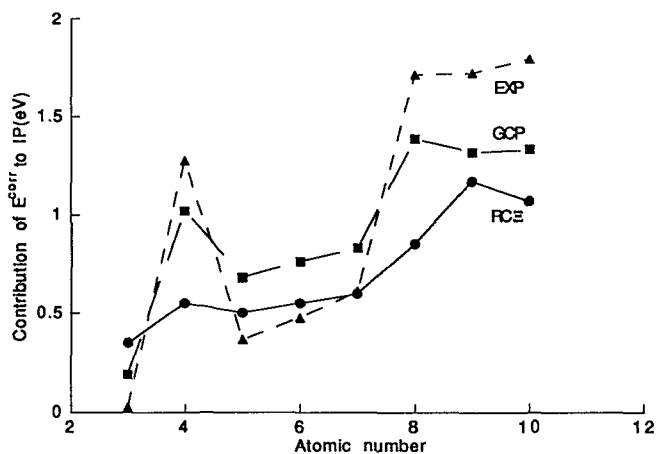


FIG. 3. Comparison of contribution of correlation energy to ionization potentials by various methods.

and, hence, the pair-correlation energy is less compared to that for Be, where two electrons are present in the outer shell. For B, C, and N, as there are no paired electrons in the outer  $p$  orbitals, there is a decrease in the contribution compared to that of Be. However, for other atoms in the first row such as O, F, and Ne, once again the contribution increases as expected, due to the presence of the paired  $p$  electrons. These general trends predicted by the GCP method are also essentially reproduced by the present method. The correlation contributions to first IP's of first row elements are thus explained based on the electronic configuration of these elements.

By using the similar arguments, we now explain the contributions to IP's for other atoms. In order to explain them, based on the electronic configurations, the elements are grouped and the contribution of correlation energy to the IP's of elements in different groups are shown in Figs. 4–6. The electronic configurations corresponding to these groups are also shown in Figs. 4–6.

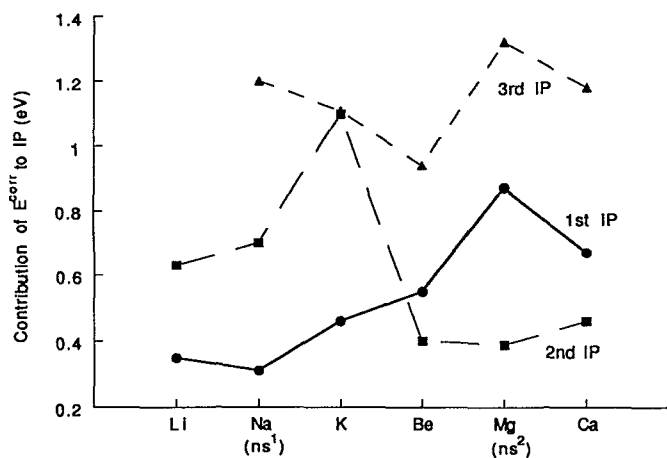


FIG. 4. Comparison contribution of correlation energy by the present RCE method to ionization potentials of atoms (Li, Na, K) and (Be, Mg, Ca).

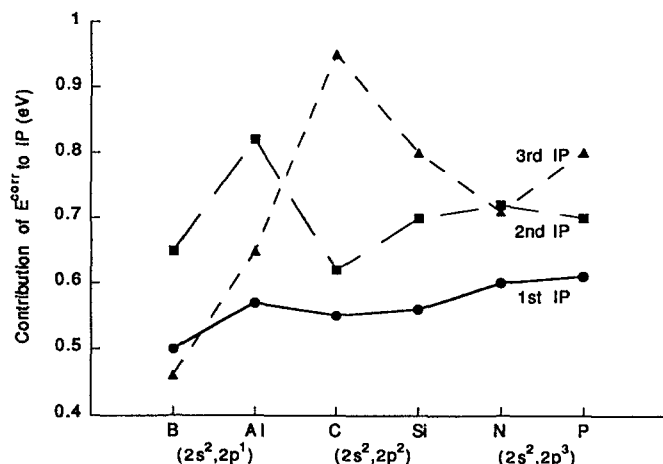


FIG. 5. Comparison contribution of correlation energy by the present RCE method to ionization potentials of atoms (B, Al), (C, Si), and (N, P).

In Fig. 4, for I A group elements such as Li, Na, and K and for II A group elements such as Be, Mg, and Ca, the correlation energy contribution to I, II, and III IP's are shown. It is seen from Fig. 4 that the  $\Delta E_I$  for I A group elements are less than those for II A group elements; it may be due to the presence of only one electron in the outer shell for the elements in I A group and so the pair-correlation energy is less while for II A group, there are more than one electron in the outer shell and, hence, the pair correlation is high.

However, the  $\Delta E_{II}$  for the I A group is larger than those for the II A group elements (see Fig. 4); this is due to the fact that the removal of an electron from the elements of I A group results in a closed-shell configuration and, hence, the pair-correlation energy is large; while for the II A group, after the pair-correlation energy is large; and while for the II A group, after the first ionization, there is only one electron in the outer shell and hence the pair correlation is less. This is why for the II A group

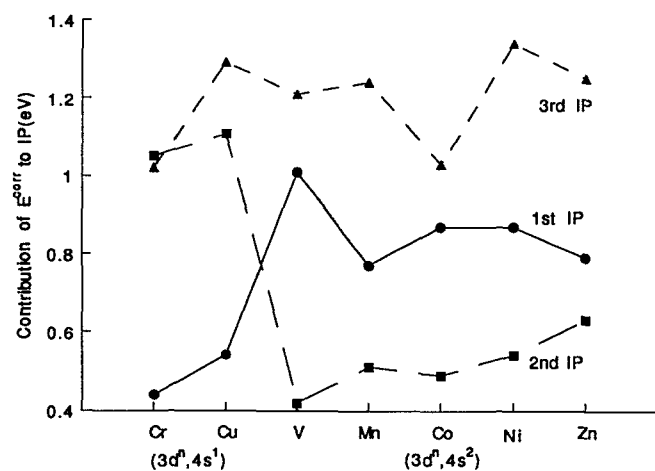


FIG. 6. Comparison contribution of correlation energy by the present RCE method to ionization potentials of atoms (Cr, Cu) and (V, Mn, Ni, Zn).

elements, the  $\Delta E_I$  is larger than the  $\Delta E_{II}$ . After the second ionization, the number of electrons in the outer shell become more than one for these I A and II A group elements and, hence, the  $\Delta E_{III}$  are larger than the contribution of correlation energy to the I and II ionization potentials.

We now compare the  $\Delta E_I$ ,  $\Delta E_{II}$ ,  $\Delta E_{III}$  for the III B group elements such as B and Al, IV B group elements such as C and Si, and elements in the V B group such as N and P. The correlation energy contribution to IP's of these elements are shown in Fig. 5. The  $\Delta E_I$ 's for the III B, IV B, and V B group elements are almost the same since there are no unpaired electrons in the outer shell.

After the first ionization the outer electronic configuration of the III B, IV B, and V B group elements become  $(ns^2)$ ,  $(ns^2, np^1)$ , and  $(ns^2, np^2)$ , respectively. The contribution of correlation to the second ionization potential  $\Delta E_{II}$  is higher for III B group elements due to the presence of unpaired electrons than for IV B and V B group elements. After the second ionization, the outer electronic configuration of the III B, IV B, and V B group elements become  $(ns^1)$ ,  $(ns^2)$ , and  $(ns^2, np^1)$ , respectively. As expected, the  $\Delta E_{III}$  for IV B group is larger than the  $\Delta E_{III}$  for the III B and V B group elements.

So far, we have discussed the contribution of correlation energy to ionization potentials by comparing the different groups. However, within the same group,  $\Delta E_I$ ,  $\Delta E_{II}$ , and  $\Delta E_{III}$  values do not seem to show any regular trend (see Figs. 4 and 5).

We now discuss the correlation energy contribution to IP's of transition metals (see Fig. 6). We have grouped the transition elements into two sets, viz., Cr and Cu in one set with electronic configuration  $(3d^n, 4s^1)$  and V, Mn, Co, Ni,

and Zn in the other set with electronic configuration  $(3d^n, 4s^2)$ . Here, in order to calculate the first IP, we have removed an electron from the 4s orbital of the transition metals. As expected, the  $\Delta E_I$  for Cr and Cu are less compared to the  $\Delta E_I$  for the remaining elements for which it is almost the same. However, for the second ionization potential, the correlation energy contribution in Cr and Cu is large, as expected, compared to that of the remaining transition elements, and also to the  $\Delta E_I$  of the same elements. The  $\Delta E_{III}$  for these atoms are larger than  $\Delta E_I$  and  $\Delta E_{II}$  of these elements as anticipated except in the case of Cr. In conclusion, successive ionization potentials are considerably affected by the correlation and contribution of correlation energy to IP's is reasonably explained on the basis of the pair-correlation energy.

<sup>1</sup>G. Kemister and S. Nordholm, *J. Chem. Phys.* **83**, 5263 (1985).

<sup>2</sup>M. T. Carroll, R. F. W. Bader, and S. H. Vosko, *J. Phys. B* **20**, 3599 (1987).

<sup>3</sup>B. O. Roos, M. Szulkin, and M. Jaszunski, *Theor. Chim. Acta.* **71**, 375 (1987).

<sup>4</sup>J. P. Perdew and A. Zunger, *Phys. Rev. B* **23** 5048 (1981).

<sup>5</sup>A. Savin, H. Stoll, and H. Preuss, *Theor. Chim. Acta* **70**, 407 (1986).

<sup>6</sup>L. A. Cole and J. P. Perdew, *Phys. Rev. A* **25**, 1265 (1982); C. F. Fischer, J. B. Lagowski, and S. H. Vosko, *Phys. Rev. Lett.* **59**, 2263 (1987); Y. Guo and M. A. Whitehead, *Phys. Rev. A* **40**, 28 (1989).

<sup>7</sup>M. Vijayakumar, N. Vaidehi, and M. S. Gopinathan, *Phys. Rev. A* **40**, 6834 (1989).

<sup>8</sup>T. Kato, *Commun. Pure Appl. Math.* **10**, 151 (1957).

<sup>9</sup>R. McWeeny, *New World of Quantum Chemistry, Proceedings of the Second International Congress of Quantum Chemistry*, edited by B. Pullman and R. G. Parr (Reidel, Boston, 1976).

<sup>10</sup>M. Vijayakumar, N. Vaidehi, and M. S. Gopinathan (unpublished).

<sup>11</sup>*CRC Handbook of Chemistry and Physics*, 68th ed. (CRC Press, Boca Raton, FL, 1987).

<sup>12</sup>J. P. Perdew, *Phys. Rev. B* **33**, 8822 (1986).