July, 1984] *Bull. Chem. Soc. Jpn.,* ***57****, 1789—1794 (1984)* 1789

Simple Estimation of Ionization Energies. An Improvement of Koopmans' Approximation by Scaling

Makoto Isihara
Department of General Education, Shotoku-Gakuen Women's Junior College,
Nakauzura 1-38, Gifu 500
(Received February 13, 1984)

A simple method of estimating ionization energies is proposed, formulation being made for atomic systems. The method aims at improving Koopmans' approximation by incorporating a scale factor into Koopmans' variation problem for the hole state in the space built of the occupied Hartree-Fock manifold of the parent state. The shrinking of the electronic cloud through ionization is effectively taken into account with the scale factor; the scaling makes the hole state fulfil the virial theorem. Numerical examples are given for valence-shell and core ionizations of several atomic systems. The results are encouraging on the whole. The attendant concepts, the quasiparticle ejection energy and the global correction, seem to be helpful in understanding the electronic behavior through ionization.

The ionization energy can be obtained, in principle, by subtracting the parent state energy from the hole state one calculated separately;[1] the problem is thus ascribed to the calculation of state energies with sufficient accuracy. Surely this way of thinking is orthodox, but we have to endure two disadvantages. One is not essential but practical; the laboriousness to keep high accuracy through subtraction of two nearly equal large numbers. The other is conceptual; the loss of intuitive and intimate understanding of the ionization energy as a physical quantity. Here it is neither suitable nor possible to give an adequate bibliography of state energy calculations;[2] we only list a few interesting devisals[3,4] and a practical approximate method based on the Rayleigh-Schrödinger perturbation theory[5] in references.

Nowadays we already have several elaborate methods of directly evaluating ionization energies of atoms and molecules, the Green's function methods,[6–10] the equation-of-motion methods,[11,12] and so on.[13,14] The perturbation analysis has arrived at a fairly high stage.[13,15,16] All of these elaborate methods, however, require relevant knowledge of unoccupied orbitals in order to display their own superior abilities; the knowledge is almost exclusively unavailable from the Hartree-Fock (HF) calculation for the parent state.

As a standard method without use of explicit knowledge of unoccupied orbitals we have what is called ΔSCF method.[17,18] Subtraction of two nearly equal large numbers being avoided in its variant the transition operator method for the ΔSCF calculation,[19] we must still perform separate self-consistent-field (SCF) calculations for each hole state of interest besides the parent state. Though ΔSCF method is a natural approximation to "separate energy calculations for individual states" mentioned above, its essential consists in meticulous consideration of the electronic reorganization effect with complete neglect of the correlation energy change; we can sometimes obtain rather comfortable estimates from Koopmans' relation[20] because of fortunate cancellation between the reorganization and correlation corrections.

Of course, we should rely on elaborate methods to reproduce or to predict experimental values accurately.[10] Simple or, in another word, handy estimations are, nevertheless, not to be despised from both practical and conceptual points of view. Especially, those of clear physical grounds advance our knowledge of both the quantity and the system under consideration.

Koopmans' relation results from the variation problem within the hole state space built of the occupied HF manifold of the parent state.[20–22] An extension to the case of the correlated parent state has been attempted[22] and analyzed.[23] Now cannot we effectively enrich Koopmans' variation problem only by introducing some additional variation parameter?

In this paper, confining ourselves to atomic systems, we propose a simple method of estimating ionization energies, where a scale factor[24] is incorporated into Koopmans' variation problem as an additional variation parameter. The motivation stems from the observation that the hole state in Koopmans' treatment does not fulfil the virial theorem[24,25] which we think a fundamental requisite for approximate states to be well-behaved. The scaling to make the virial theorem hold in the hole state is a key of the present method. Our confinement to atomic systems should not be regarded as an intrinsic restriction but is a setting for the compact presentation of the essential of the method.

Method

Throughout this section we work within the spin unrestricted picture, calling spinorbitals merely orbitals. Let $\{\phi_p\}$ be canonical orbitals obtained from the HF calculation for the parent state. The scaled orbitals $\{\phi_p^\lambda\}$ are constructed with a real scale factor λ as

$$\phi_p^\lambda(\boldsymbol{r}) = \lambda^{3/2}\phi_p(\lambda\boldsymbol{r}), \tag{1}$$

where $\boldsymbol{r}$ stands for the spatial coordinate. The orthonormality is preserved in the sense that

$$\int \phi_p^{\lambda *}\phi_q^\lambda \mathrm{d}\tau = \delta_{pq}, \tag{2}$$

the integration running over the spin and spatial coordinates. Denoting the creation and annihilation operators for ϕ_p^λ as $a_p^{\lambda\dagger}$ and a_p^λ, respectively, we can write the electronic Hamiltonian in the second quantized form as

$$H = \sum_{pq} (\lambda^2 t_{pq} + \lambda v_{pq}) a_p^{\lambda\dagger} a_q^{\lambda} + \frac{\lambda}{2} \sum_{pqrs} v_{qs}^{pr} a_p^{\lambda\dagger} a_r^{\lambda\dagger} a_s^{\lambda} a_q^{\lambda}, \tag{3}$$

where

$$t_{pq} = \int \phi_p^* (-\Delta/2) \phi_q \mathrm{d}\tau, \tag{4}$$

$$v_{pq} = \int \phi_p^* (-Z/|\boldsymbol{r}|) \phi_q \mathrm{d}\tau, \tag{5}$$

and

$$v_{qs}^{pr} = \iint \phi_p^*(\boldsymbol{r}) \phi_r^*(\boldsymbol{r}') (1/|\boldsymbol{r}-\boldsymbol{r}'|) \phi_s(\boldsymbol{r}') \phi_q(\boldsymbol{r}) \mathrm{d}\tau \mathrm{d}\tau'. \tag{6}$$

Here Z is the atomic number.

Let us label the occupied orbitals in the parent state with the indices $\{i, j, k, l\}$ and introduce the notation for the scaled HF state

$$|N,\lambda\rangle = \prod_j a_j^{\lambda\dagger} |\text{vacuum}\rangle. \tag{7}$$

The parent state, written in the above notation as $|N,1\rangle$, has the energy

$$E_N = \langle N,1|H|N,1\rangle = T + V \tag{8}$$

with

$$T = \sum_j t_{jj} \tag{9}$$

and

$$V = \sum_j (v_{jj} + \sum_k (v_{jk}^{jk} - v_{kj}^{jk})/2). \tag{10}$$

We postulate that the parent state already satisfies the virial theorem;[25)]

$$2T + V = 0. \tag{11}$$

On the other hand, our trial hole state is prepared in the form

$$|N-1,\lambda,\boldsymbol{C}\rangle = \sum_j c_j^* a_j^{\lambda} |N,\lambda\rangle, \tag{12}$$

where $\boldsymbol{C}$ stands for $\{c_j\}$. This trial state is, of course, orthogonal to the parent state $|N,1\rangle$, since they are different eigenstates of the number of electrons. Regarding λ and $\boldsymbol{C}$ as variation parameters, we would like to minimize the expectation value

$$\begin{aligned} E_{N-1}(\lambda,\boldsymbol{C}) &= \langle N-1,\lambda,\boldsymbol{C}|H|N-1,\lambda,\boldsymbol{C}\rangle \\ &= \lambda^2 (T - \sum_{jk} c_j^* c_k t_{jk}) + \lambda (V - \sum_{jk} c_j^* c_k u_{jk}) \end{aligned} \tag{13}$$

with

$$u_{jk} = v_{jk} + \sum_l (v_{kl}^{jl} - v_{lk}^{jl}) \tag{14}$$

under the normalization constraint

$$\langle N-1,\lambda,\boldsymbol{C}|N-1,\lambda,\boldsymbol{C}\rangle = \sum_j c_j^* c_j = 1. \tag{15}$$

This conditional extremum problem can be treated easily as an unconditional one by Lagrange's undetermined multiplier method. Noting that $\{t_{jk}\}$ and $\{u_{jk}\}$ are hermitian, we resultantly arrive at the following system of equations with a real multiplier ω.

$$\begin{cases} \lambda = \left(-\dfrac{1}{2}\right)(V - \sum_{jk} c_j^* c_k u_{jk}) / (T - \sum_{jk} c_j^* c_k t_{jk}) & (16) \\ \sum_k (\lambda^2 t_{jk} + \lambda u_{jk}) c_k = \omega c_j & (17) \end{cases}$$

together with the normalization condition given by Eq. 15.

Because λ contains $\boldsymbol{C}$, Eq. 17 does not form a genuine eigenvalue problem. It is, however, impractical to work out the problem by substituting Eq. 16 into Eq. 17. We had better solve the system of Eqs. 16 and 17 iteratively, treating Eq. 17 as an eigenvalue problem with λ given:

[0] For certain i, assume the mixing coefficients as

$$c_j = \delta_{ji}. \tag{18}$$

[1] Compute λ by Eq. 16 with the assumed $\boldsymbol{C}$.

[2] Solve the eigenvalue problem Eq. 17 for the computed λ, obtaining the computed $\boldsymbol{C}$ through the normalization of Eq. 15.

[3] Go back to the process 1 with the computed $\boldsymbol{C}$ as the assumed $\boldsymbol{C}$ until the computed $\boldsymbol{C}$ coincides with the assumed $\boldsymbol{C}$.

As to usual ionization energies we may choose the index of the highest occupied orbital as i in the initial setting (Eq. 18). Other choices of i lead us to inner valence-shell and core ionization energies.

Our hole state thus obtained fulfils the virial theorem; Eq. 16 is nothing other than the virial condition.[25)] After substitution of the determined λ and $\boldsymbol{C}$, Eq. 13 gives the hole state energy

$$E_{N-1} = \lambda^2 T + \lambda V - \omega \tag{19}$$

by virtue of Eq. 17. From Eqs. 8 and 19, using the virial theorem for the parent state (Eq. 11), we have the ionization energy

$$I = E_{N-1} - E_N = -\omega + \Lambda \tag{20}$$

with

$$\Lambda = -(\lambda - 1)^2 E_N. \tag{21}$$

In the form of Eq. 20 a characteristic of our method is clearly seen. Our ionization energy consists of two parts: $-\omega$, the ejection energy of the quasiparticle for the ionization considered, literally of quasiparticle nature, and Λ, the residual correction, of global nature. It may be suitable and convenient to refer to the former as the quasiparticle ejection energy and to the latter as the global correction. Note that the scaling affects not only Λ of the explicit λ-dependence but also ω. Roughly speaking, the scale factor greater than unity shrinks the electronic cloud closer to the nucleus. This contraction conserves the "shape" of the electronic cloud for the constituent hole state $a_j^{\lambda}|N,\lambda\rangle$ individually, but the image of the shape-conservative contraction fails in the hole state $|N-1,\lambda,\boldsymbol{C}\rangle$ in general, because λ and $\boldsymbol{C}$ interrelate to each other.

Without scaling, that is, in Koopmans' treatment, we have Eq. 17 with $\lambda=1$, which is just the canonical HF equation in the canonical orbital representation; ω becomes the canonical orbital energy and Λ vanishes. Still Koopmans' approximation is not to be confused with a "limiting case" of making λ tend to unity in our method. The approximation inherently violates the virial theorem for the hole state.

Numerical Examples

The present method has been applied to valence-shell and core ionizations of several atomic systems of which parent states have single configurations in Roothaan's

TABLE 1. DEPENDENCE ON THE SIZE OF A BASIS SET

System	B_N[a)]	E_N^{SCF}[b)]/a.u.	1s-ionization		2p-ionization	
			I/a.u.	λ	I/a.u.	λ
He	1	−2.84766	0.8477	1.18519		
	2	−2.86167	0.8720	1.17922		
	5	−2.86168	0.8720	1.17921		
Ne	1, 1 [1]	−127.812	32.144	1.07603	0.5358	1.01449
	2, 2 [2]	−128.535	32.247	1.07540	0.8179	1.01375
	2, 3 [4]	−128.547	32.261	1.07536	0.8270	1.01374
	2, 4 [4]	−128.547	32.261	1.07536	0.8270	1.01374
Ar	1, 1, 1 [1, 1]	−525.765	117.77	1.04165	9.211	1.01452
	2, 2, 2 [2, 2]	−526.815	117.83	1.04377	9.468	1.01414
	2, 2, 3 [2, 3]	−526.817	117.83	1.04378	9.469	1.01415
	1, 0, 7 [1, 0, 7]	−526.817	117.83	1.04379	9.470	1.01416

a) The number of the basis functions for the parent state SCF calculation; $n_1,n_2,\cdots[n_3,n_4,\cdots]$ means $n_1\times 1\mathrm{s}+n_2\times 2\mathrm{s}+\cdots n_3\times 2\mathrm{p}+n_4\times 3\mathrm{p}+\cdots$. b) The SCF parent state energy.

TABLE 2. DEPENDENCE ON THE BASIS SET OF THE SIMILAR SIZE

System		Na^+		Cl^-			
Ionization		1s	2p	1s	2s	2p	3s
B[a,b)]	K[d)]/a.u.	40.760	1.7929	104.51	10.229	7.6956	0.7332
	I/a.u.	40.231	1.7701	103.74	10.150	7.6007	0.7305
	λ	1.06768	1.01319	1.04652	1.01376	1.01465	1.00246
	C 1s	0.99947		0.99969	−0.00682		0.00031
	2s [2p]	0.03261	[1.00000]	0.02408	0.99992	[0.99995]	−0.00187
	3s [3p]			−0.00625	0.01074	[0.00965]	1.00000
CR[b,c)]	K/a.u.	40.760	1.7972	104.51	10.229	7.6953	0.7330
	I/a.u.	40.232	1.7700	103.74	10.150	7.6004	0.7302
	λ	1.06768	1.01319	1.04652	1.01376	1.01464	1.00245
	C 1s	0.99947		0.99969	−0.00682		0.00031
	2s [2p]	0.03262	[1.00000]	0.02408	0.99992	[0.99995]	−0.00184
	3s [3p]			−0.00625	0.01072	[0.00965]	1.00000

a) The case of Bagus' bases: $B_N=2,2,1[4]$ for Na^+ and 1,2,4[3,2,2] for Cl^-. b) Both of Bagus' and CR's bases give E_N^{SCF}/a.u.$=-161.677$ for Na^+ and -459.577 for Cl^-. c) The case of CR's bases: $B_N=2,3[4]$ for Na^+ and 2,2,3[2,4] for Cl^-. d) Koopmans' value.

HF calculation.[26)] The results are summarized in Tables 1—5.

Tables 1 and 2 concern preliminary examination of the basis set dependence. The dependence on the size of a basis set is examined in Table 1 using Clementi and Roetti (CR)'s bases.[27)] As the result of SCF calculation settles down, that of our calculation also does. There is an obvious gap between the single and double zeta results; the former seems of no use. Table 2 compares the cases using CR's and Bagus'[17)] bases of the similar size. The results are almost identical. As the SCF calculation tends to the HF limit, this identity is expected to become complete. What is shown in Tables 1 and 2 is rather natural, since our method does not work upon basis functions themselves but work upon occupied HF orbitals.

Table 3 presents the results for usual valence-shell ionizations. CR's occupied SCF orbitals are used as a starting point of our calculation. Koopmans' and the ΔSCF values for the sake of comparison are quoted also from CR's SCF calculation. For the closed-shell systems, that is, for He-, Ne-, and Ar-isoelectronic systems, our values of ionization energies are variously lower than Koopmans' ones, nearing the experimental; the lowering ranges from about eighty to a few percent of that attained by ΔSCF method. On the other hand, for what we call the semiclosed-shell systems, Be- and Mg-isoelectronic systems, our values are only little depressed from and remain approximately equal to Koopmans' values in spite of the obvious lowering of the ΔSCF values. The ionization energies of these systems are, as is well known, rather considerably larger than Koopmans' estimates; our method can be said to work fairly well. The results for the open-shell systems, N and O^+, are moderate and we may draw no outstanding feature from them; our estimates are a little more agreeable than Koopmans' ones.

Tables 4 and 5 show the results for core ionizations.

TABLE 3. IONIZATION ENERGIES OF ATOMIC SYSTEMS a)

System	He	Li$^+$	Be	B$^+$	N b)	O$^+$ b)	F$^-$
B_N	5	4	2, 4	2, 3	2, 4 [4]	2, 3 [4]	2, 3 [5]
B_{N-1} c)	hy. d)	hy.	2, 2	2, 2	2, 3 [4]	2, 3 [4]	2, 4 [4]
Δ e) /a.u.	0.8617	2.736	0.296	0.862	0.513	1.273	0.050
K/a.u.	0.9180	2.7924	0.3093	0.8738	0.5676	1.3269	0.1809
X e, f) /a.u.	0.90354	2.7796	0.3426	0.92437	0.53410	1.2905	0.129†
I/a.u.	0.8720	2.7453	0.3086	0.8728	0.5594	1.3166	0.1622
ω/a.u.	0.7801	2.6510	0.3079	0.8718	0.5509	1.3058	0.1430
Λ/a.u.	0.0919	0.0943	0.0007	0.0010	0.0085	0.0108	0.0192
λ	1.17921	1.11414	1.00709	1.00664	1.01246	1.01204	1.01389
C 1s	1.00000	1.00000	−0.00246	−0.00271			
2s [2p]			1.00000	1.00000	[1.00000]	[1.00000]	[1.00000]
R g)	81.7	83.5	5.3	8.5	15.0	19.1	14.3
$D\Delta$ h) /a.u.	−0.0418	−0.044	−0.047	−0.062	−0.021	−0.018	−0.079
DK h) /a.u.	0.0145	0.0128	−0.0333	−0.0506	0.0335	0.0364	0.052
DI h) /a.u.	−0.0315	−0.0343	−0.0340	−0.0516	0.0253	0.0261	0.033

System	Ne	Na$^+$	Mg	Al$^+$	Cl$^-$	Ar	K$^+$
B_N	2, 4 [4]	2, 3 [4]	2, 2, 3 [3]	2, 2, 3 [3]	2, 2, 3 [2, 4]	2, 2, 3 [2, 3]	2, 2, 3 [2, 3]
B_{N-1}	2, 3 [4]	2, 3 [4]	2, 2, 3 [3]	2, 2, 3 [3]	2, 2, 3 [2, 3]	2, 2, 3 [2, 3]	2, 2, 3 [2, 3]
Δ/a.u.	0.729	1.680	0.242	0.644	0.095	0.543	1.126
K/a.u.	0.8504	1.7972	0.2530	0.6521	0.1499	0.5906	1.1711
X/a.u.	0.79244	1.7377	0.2810	0.69190	0.136†	0.57912	1.1622
I/a.u.	0.8270	1.7700	0.2529	0.6519	0.1481	0.5885	1.1680
ω/a.u.	0.8028	1.7419	0.2528	0.6517	0.1462	0.5860	1.1648
Λ/a.u.	0.0242	0.0281	0.0001	0.0002	0.0019	0.0025	0.0032
λ	1.01374	1.01319	1.00073	1.00092	1.00202	1.00219	1.00229
C 1s			0.00005	0.00010			
2s [2p]	[1.00000]	[1.00000]	−0.00040	−0.00061	[−0.00130]	[−0.00158]	[−0.00170]
3s [3p]			1.00000	1.00000	[1.00000]	[1.00000]	[1.00000]
R	19.3	23.2	0.9	2.5	3.3	4.4	6.9
$D\Delta$/a.u.	−0.063	−0.058	−0.039	−0.048	−0.041	−0.036	−0.036
DK/a.u.	0.0580	0.0595	−0.0280	−0.0398	0.014	0.0115	0.0089
DI/a.u.	0.0346	0.0323	−0.0281	−0.0400	0.012	0.0094	0.0058

a) The valence-shell ionization concerning the highest occupied orbital is meant. b) The ^4S state is used as the parent state. c) The number of the basis functions for the hole state SCF calculation in ΔSCF method. d) The hydrogen-like orbital. e) Δ and X stand for the ΔSCF and experimental values, respectively. f) All values are taken from the table in Ref. 28 except for the values with a dagger, which are from the data of electron affinities (Ref. 29). g) The percentage of the lowering from Koopmans' value by the present method in that by ΔSCF method; $R=100(K-I)/(K-\Delta)$. h) The deviations from the experimental value; $D\Delta=\Delta-X$, $DK=K-X$, and $DI=I-X$.

Occupied orbitals for our calculation as well as Koopmans' and the ΔSCF values are taken from Bagus' SCF calculation. Certainly ΔSCF method gives much more excellent results than Koopmans' relation as to core ionizations in which the reorganization effect is primary.[17,18] The present method works satisfactorily as well for inner core ionizations. For outer core ionizations,[18] however, our values are not so favorable, being better than Koopmans' to some extent.

The global correction is generally small and about few percent or less of the ionization energy, yet the magnitude is usually comparable with the difference between Koopmans' and experimental values of the ionization energy. We have the slight global corrections due to the scale factors very close to unity for the valence-shell ionizations of the semiclosed-shell systems. This seems, so to speak, to represent the "stiffness" of the electronic cloud characteristic of these systems. Another general feature is observed in the results of the isoelectronic sequence: While the quasiparticle ejection energy changes distinctly according to the atomic number in a sequence, the global correction as well as the scale factor varies comparatively slowly. As the atomic number increases, the scale factor becomes small little by little remaining similar. This may be well understood from the image that the larger nuclear charge forms the tighter electronic cloud with the similar shape in the parent

TABLE 4. THE 1s-IONIZATION ENERGIES OF Ne- AND Ar-ISOELECTRONIC SYSTEMS

System	F^-	Ne	Na^+	Cl^-	Ar	K^+
B_N	2, 3, 1 [5]	2, 2, 1 [4]	2, 2, 1 [4]	1, 2, 4 [3, 2, 2]	1, 2, 4 [3, 2, 2]	1, 2, 4 [3, 2, 2]
B_{N-1}	2, 2, 1 [4]	2, 2, 1 [4]	2, 2, 1 [4]	1, 2, 4 [3, 2, 2]	1, 2, 4 [3, 2, 2]	1, 2, 4 [3, 2, 2]
Δ/a.u.	24.935	31.921	39.935	103.29	117.43	132.59
K/a.u.	25.830	32.772	40.760	104.51	118.61	133.75
$X^{a)}$/a.u.	24.992	31.985*	40.000	103.60	117.81*	133.10
I/a.u.	25.345	32.261	40.231	103.74	117.83	132.96
ω/a.u.	24.640	31.531	39.491	102.75	116.82	131.94
Λ/a.u.	0.705	0.730	0.740	0.99	1.01	1.02
λ	1.08421	1.07536	1.06768	1.04652	1.04379	1.04127
C 1s	0.99924	0.99937	0.99947	0.99969	0.99972	0.99975
2s	0.03894	0.03559	0.03261	0.02408	0.02278	0.02155
3s				−0.00625	−0.00624	−0.00621
R	54.2	60.1	64.1	63.1	66.1	68.1
$D\Delta$/a.u.	−0.057	−0.064	−0.065	−0.31	−0.38	−0.51
DK/a.u.	0.838	0.787	0.760	0.91	0.80	0.65
DI/a.u.	0.353	0.276	0.231	0.14	0.02	−0.14

a) The values with an asterisk are taken from the table in Ref. 30; others are from Bagus' paper, Ref. 17.

TABLE 5. THE 2s-IONIZATION ENERGIES OF Ne- AND Ar-ISOELECTRONIC SYSTEMS

System	F^-	Ne	Na^+	Cl^-	Ar	K^+
B_N	2, 3, 1 [5]	2, 2, 1 [4]	2, 2, 1 [4]	1, 2, 4 [3, 2, 2]	1, 2, 4 [3, 2, 2]	1, 2, 4 [3, 2, 2]
B_{N-1}	2, 2, 1 [4]	2, 2, 1 [4]	2, 2, 1 [4]	1, 2, 4 [3, 2, 2]	1, 2, 4 [3, 2, 2]	1, 2, 4 [3, 2, 1]
Δ/a.u.	0.9282	1.8123	2.9682	9.811	11.938	14.346
K/a.u.	1.0746	1.9303	3.0737	10.229	12.322	14.708
X/a.u.	0.8947	1.7812*	2.9434	9.7?	11.99*	14.4?
I/a.u.	1.0529	1.9075	3.0496	10.150	12.237	14.620
ω/a.u.	1.0293	1.8824	3.0232	10.063	12.145	14.523
Λ/a.u.	0.0236	0.0251	0.0264	0.087	0.092	0.097
λ	1.01541	1.01397	1.01279	1.01376	1.01325	1.01271
C 1s	−0.00646	−0.00606	−0.00572	−0.00682	−0.00662	−0.00639
2s	0.99998	0.99998	0.99998	0.99992	0.99992	0.99992
3s				0.01074	0.01083	0.01076
R	14.8	19.3	22.8	18.9	22.1	24.3
$D\Delta$/a.u.	0.0335	0.0331	0.0248	0.1	−0.05	−0.1
DK/a.u.	0.1799	0.1491	0.1303	0.5	0.33	0.3
DI/a.u.	0.1582	0.1263	0.1062	0.4	0.25	0.2

state. The scale factor and the global correction reflect a nature of the electronic cloud of the system considered.

Concluding Remarks

The method proposed is a natural improvement of Koopmans' approximation but stands on a much more sound ground. The numerical examples in the previous section show the usefulness of the method in both qualitative and quantitative aspects. Though the method, intended for a handy estimation, should not be expected to reproduce experimental values accurately, the obtained values are almost always better than Koopmans' and sometimes surprisingly appropriate. The method allows us to get some feel about the electronic behavior through ionization. Above all it should be emphasized that our method requires little additional work to the parent state HF calculation, the laboriousness being incomparable with that of the HF calculation for each hole state of interest. We believe that the present method is promising as a simple estimation in place of Koopmans' relation.

The idea of the present work has two obvious direction of development: One is, of course, an extension to molecular systems. We have somewhat more to be done, but there seems to exist no essential difficulty. The other is an application to estimating electron affinities, which is straightforward in principle. Still the virtual orbitals supplied by the parent state HF calculation are unphysical or poor-physical; we must improve the virtual orbitals[31] relevantly at a time.

References

1) There is some semantic problem about the usage of the terms: ground, ionic, hole states, and so on. The definition of the ground state is arbitrary depending on whether or not the number of electrons are specified (Specified: The usual ionization $\mathrm{He}\rightarrow\mathrm{He}^+$ is the process from the two-electron ground state to the one-electron ground state. Nonspecified: In the process $\mathrm{Be}^+\rightarrow\mathrm{Be}^{++}$ we cannot call Be^+ the ground state, the ground state being Be.), but the tractable N-electron state may be referred to as the ground state concerning the transition to the $N-1$-electron state. When the N-electron state is ionic, the $N-1$-electron state is not necessarily ionic. Though the "ionized" state matches the word "ionization", it is suitable to call the $N-1$-electron state the ionized state only if the N-electron state is neutral. We use "parent" for "N-electron" and "hole" for "$N-1$-electron"; the word "hole" does not always fit literally into the $N-1$-electron state. The term "ionization energy" is undoubtedly inappropriate for the ionic parent state, yet it has been used traditionally too long to be replaced by others. Here we use it reluctantly.

2) Some fundamental, important works are cited in Ref. 10b.

3) S. F. Boys and N. C. Handy, *Proc. R. Soc. London, Ser. A*, **310**, 43 (1969); *ibid.*, **310**, 63 (1969).

4) A. W. Weiss, *Phys. Rev. A*, **3**, 126 (1971); C. M. Moser and R. K. Nesbet, *ibid.*, **4**, 1336 (1971); *ibid.*, **6**, 1710 (1972).

5) D. P. Chong, F. G. Herring, and D. McWilliams, *J. Chem. Phys*, **61**, 78 (1974); their subsequent works with great attention to basis sets are cited in Ref. 10b up to 1977; D. P. Chong and S. R. Langhoff, *Chem. Phys.*, **67**, 153 (1982). For the use of energy-shifted perturbation theory, D. P. Chong and Y. Takahata, *Int. J. Quantum Chem.*, **12**, 549 (1977). For the use of effective core potentials, S. R. Langhoff and D. P. Chong, *Int. J. Quantum Chem.*, **23**, 875 (1983); *Chem. Phys. Lett.*, **100**, 259 (1983).

6) W. P. Reinhardt and J. D. Doll, *J. Chem. Phys.*, **50**, 2767 (1969); F. Ecker and G. Hohlneicher, *Theor. Chim. Acta*, **25**, 289 (1972); J. D. Doll and W. P. Reinhardt, *J. Chem. Phys.*, **57**, 1169 (1972); L. S. Cederbaum, G. Hohlneicher, and S. Peyerimhoff, *Chem. Phys. Lett.*, **11**, 421 (1971); W. P. Reinhardt and J. B. Smith, *J. Chem. Phys.*, **58**, 2148 (1973). These are pioneering works but may be said to have become rather primitive today.

7) B. Schneider, H. S. Taylor and R. Yaris, *Phys. Rev. A*, **1**, 855 (1970); B. S. Yarlagadda, G. Csanak, H. S. Taylor, B. Schneider, and R. Yaris, *ibid.*, **7**, 146 (1973); P.-O. Nerbrant, *Int. J. Quantum Chem.*, **9**, 901 (1975).

8) L. S. Cederbaum, *Theor. Chim. Acta*, **31**, 239 (1973); *J. Chem. Phys.*, **62**, 2160 (1975); *J. Phys. B*, **8**, 290 (1975). His method has produced a dominant number of applicative works, on which we refer to review articles in Ref. 10. A new approximation scheme has been proposed on Green's functions; J. Schirmer, L. S. Cederbaum, and O. Walter, *Phys. Rev. A*, **28**, 1237 (1983).

9) G. D. Purvis and Y. Öhrn, *J. Chem. Phys.*, **60**. 4063 (1974); *ibid.*, **62**, 2045 (1975).

10) a) L. S. Cederbaum and W. Domcke, *Adv. Chem. Phys.*, **36**, 205 (1977); b) W. von Niessen, G. H. F. Diercksen, and L. S. Cederbaum, *J. Chem. Phys.*, **67**, 4124 (1977).

11) J. Simons and W. D. Smith, *J. Chem. Phys.*, **58**, 4899 (1973); J. Simons, *Chem. Phys. Lett.*, **25**, 122 (1974). See the references of Ref. 10b as to its applications.

12) D. L. Yeager, Ph. D. Thesis, California Institute of Technology, 1975; M. F. Herman, K. F. Freed, and D. L. Yeager, *Adv. Chem. Phys.*, **48**, 1 (1981).

13) B. T. Pickup and O. Goscinski, *Mol. Phys.*, **26**, 1013 (1973).

14) I. Hubač, V. Kvasnička, and A. Holubec, *Chem. Phys. Lett.*, **23**, 381 (1973); V. Kvasnička and I. Hubač, *J. Chem. Phys.*, **60**, 4483 (1974).

15) A. J. Hernández and P. W. Langhoff, *Chem. Phys. Lett.*, **49**, 421 (1977).

16) G. Born, H. A. Kurtz, and Y. Öhrn, *J. Chem. Phys.*, **68**, 74 (1978).

17) P. S. Bagus, *Phys. Rev.*, **139**, A619 (1965).

18) L. Hedin and A. Johansson, *J. Phys. B*, **2**, 1336 (1969).

19) O. Goscinski, B. T. Pickup, and G. Purvis, *Chem. Phys. Lett.*, **22**, 167 (1973); O. Goscinski, M. Hehenberger, B. Roos, and P. Siegbahn, *ibid.*, **33**, 427 (1975).

20) T. Koopmans, *Physica*, **1**, 104 (1933).

21) R. K. Nesbet, *Adv. Chem. Phys.*, **9**, 321 (1965); M. D. Newton, *J. Chem. Phys.*, **48**, 2825 (1968); M. Isihara, *Bull. Chem. Soc. Jpn.*, **55**, 1392 (1982); correction, *ibid.*, **55**, 2692 (1982).

22) D. W. Smith and O. W. Day, *J. Chem. Phys.*, **62**, 113 (1975); O. W. Day and K. W. Smith, *ibid.*, **62**, 155 (1975); M. M. Morrell, R. G. Parr, and M. Levy, *ibid.*, **62**, 549 (1975).

23) B. T. Pickup, *Chem. Phys. Lett.*, **33**, 422 (1975); E. Andersen and J. Simons, *J. Chem. Phys.*, **66**, 1067 (1977).

24) P.-O. Löwdin, *J. Mol. Spectrosc.*, **3**, 46 (1959); this contains a complete bibliography of the fundamental works on the subject up to 1958; A. D. McLean, *J. Chem. Phys.*, **40**, 2774 (1964).

25) S. T. Epstein, "The Variation Method in Quantum Chemistry," Academic Press, New York (1974), Section 20.

26) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951); *ibid.*, **32**, 179 (1960).

27) E. Clementi and C. Roetti, *At. Data Nucl. Data Tables*, **14**, 177 (1974).

28) C. E. Moore, "Ionization Potentials and Ionization Limits Derived from Analyses of Optical Spectra," NSRDS-NBS 34, U. S. Government Printing Office, Washington, D. C. (1970).

29) L. M. Branscombe, "Atomic and Molecular Processes," ed by D. R. Bates, Academic Press, New York (1962), p. 135.

30) D. A. Shirley, R. L. Martin, S. P. Kowalczyk, F. R. McFeely, and L. Ley, *Phys. Rev. B*, **15**, 544 (1977).

31) For example, S. Huzinaga and C. Arnau, *Phys. Rev. A*, **1**, 1285 (1970); *J. Chem. Phys.*, **54**, 1948 (1971); E. R. Davidson, *ibid.*, **57**, 1999 (1972); K. Morokuma and S. Iwata, *Chem. Phys. Lett.*, **16**, 192 (1972); S. Huzinaga and K. Hirao, *J. Chem. Phys.*, **66**, 2157 (1977).