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Theoretical studies on the ionization potential of interacting atoms at large separations

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The theory of the one-particle Green's function is applied to calculations of the ionization potential of interacting atoms which are at large separations. Equations for the ionization potential involve terms which relate to Van der Waals interactions between separated atoms and long-range interactions between an atom and an ion. Numerical calculations of the ionization potential of two hydrogen atoms and two helium atoms at large separations are performed. Applications to the ionization potentials of weakly-interacting Van der Waals molecules (NeAr, NeKr, NeXe) are also reported.

Key words: One-particle Green's function — Ionization potential — Van der Waals interaction — Long-range interaction

1. Introduction

Thanks to the development of photoelectron spectroscopy techniques, we know the ionization potentials of many interesting atoms and molecules. To explain these, various theoretical methods of calculating the IPs of atoms and molecules have been proposed. The most familiar one uses Koopmans' theorem. Koopmans' theorem says that the IP is the absolute value of the atomic orbital energy of an atom or the molecular orbital energy of a molecule. But it is an orbital approximation and does not consider electron correlation nor orbital relaxation. Another familiar method is the ΔSCF method. The IP, according to the ΔSCF method, is the difference between the total SCF energies of the neutral system and the cationic system. The development of digital computers makes it possible to perform high level calculations for relatively small molecules. From high level CI calculations we can get good total energies for both neutral and cationic systems and the difference of their total energies gives us a reliable IP. But a high level CI calculation has a high cost and its physical meaning is not clear. Recently, new techniques of many-body theory have been applied to the calculation of IP. One of them is the Green's function method [1]. In especial Cederbaum et al. have studied the one-particle Green's function vigorously [2] and their results on the calculation of IPs of various molecules by the Green's function are in good agreement with the experimental IPs. The merits of the Green's function for the calculation of the IP are:

(1) We can get the IP directly (the subtraction of total energies is apt to be accompanied with non-negligible computational errors).

(2) Physical interpretation of the IP is clear.

(3) The number of two-electron integrals which we need to calculate is much smaller than using CI.

A Green's function calculation costs less than CI and the reliability of its results is comparable with that of CI. In the present work, the Green's function is used to calculate the IP of interacting atoms which are at large separations. Cederbaum et al. used perturbative expansions of the Green's function for their calculations of the IP of molecules. We also do this by using atomic orbitals to construct the zero-th order Green's matrix. We assume that the distance apart of the two atoms is large enough for exchange effects to be ignored. But the Van der Waals force implies that each atom acts on the other and instantaneously polarizes its atomic orbitals. We derive the equation for the IP of the system of two polarized atoms by using the perturbation formula for the Green's function to second order (Sect. 2). Though the truncation of the perturbation is of low order, we can get a clear physical interpretation of the ionization process of this system (Sect. 3). The equations for the IP involve Van der Waals interaction terms between atoms and long-range interaction terms between an atom and an ion. In Sects. 4 and 5 we examine two simple examples. One is a pair of hydrogen atoms at large separations. The other consists of two helium atoms at large separations. In this case the IP has not only long-range interaction terms but also electron correlation and orbital relaxation terms of the atom from which an electron has been ejected. We also performed CI calculations and compared these results. In Sect. 6 we apply our physical interpretation to the IPs of weakly-interacting Van der Waals molecules (NeAr, NeKr, NeXe).

2. One-particle Green's functions

The Fourier transform of the one-particle Green's function is determined from the equation [3]

$$G = G_0 + G_0 \Sigma G, \tag{1}$$

where Σ is the self-energy and G_0 is the zero order approximation. When we take a Slater determinant of Hartree–Fock orbitals as the ground-state N-electron wave function, ε_k are the Hartree–Fock orbital energies and G_0 is the diagonal matrix:

$$G_{0kl}=\frac{\delta_{kl}}{\omega-\varepsilon_k}. \tag{2}$$

Equation (1) is rewritten as

$$G^{-1}=G_0^{-1}-\Sigma \tag{3}$$

and its diagonal and off-diagonal matrix elements are

$$G_{kk}^{-1}=\omega-\varepsilon_k-\Sigma_{kk} \tag{4}$$

$$G_{kl}^{-1}=-\Sigma_{kl} \quad (k\neq l). \tag{5}$$

Now consider the system consisting of two atoms at large separations. There are two atoms A and B, and each atom has its Hartree–Fock atomic orbitals $\{\varphi_1^A, \varphi_2^A, \ldots, \varphi_i^A\}$ for A, $\{\varphi_1^B, \varphi_2^B, \ldots, \varphi_j^B\}$ for B, where $i+j=N$. If the distance between A and B is large enough for the overlap integrals to be ignored, $\{\varphi_1^A, \varphi_2^A, \ldots, \varphi_i^A; \varphi_1^B, \varphi_2^B, \ldots, \varphi_j^B\}$ form an orthonormal basis set. This basis set is adapted to the atoms and not to the molecule. We can use these to construct the ground-state N-electron wave function

$$\Psi_0^N=\left|\varphi_1^{\mathrm{A}}, \varphi_2^{\mathrm{A}}, \ldots, \varphi_i^{\mathrm{A}}; \varphi_1^{\mathrm{B}}, \varphi_2^{\mathrm{B}}, \ldots, \varphi_j^{\mathrm{B}}\right|. \tag{6}$$

We estimate the self-energy Σ by the usual diagrammatic method, with the expansion to second order

$$\Sigma=\Sigma^{(1)}+\Sigma^{(2)}. \tag{7}$$

We assume that the distance between A and B is so large that we can regard the overlap and exchange integrals between A and B as zero. The first order term $\Sigma^{(1)}$ is zero because of the spherically symmetric electron distribution of each atom. Also, in the second order terms, the ω-independent terms become zero and we need the ω-dependent diagrams.

The result is as follows (where $p, q \in \mathrm{A}$ and the indices i, j, l stand for doubly occupied orbitals and a, b, c for unoccupied orbitals)

$$\Sigma_{pq}^{(2)}(\omega)=\sum_{i,l,a\in\mathrm{A}}\frac{(2V_{pail}-V_{pali})V_{qail}}{\omega+\varepsilon_a-\varepsilon_i-\varepsilon_l}+\sum_{i,a,b\in\mathrm{A}}\frac{(2V_{piab}-V_{piba})V_{qiab}}{\omega+\varepsilon_i-\varepsilon_a-\varepsilon_b} \tag{8a}$$

$$+\sum_{\substack{i\in\mathrm{A}\\ j,c\in\mathrm{B}}}\frac{2V_{pcij}V_{qcij}}{\omega+\varepsilon_c-\varepsilon_i-\varepsilon_j}+\sum_{\substack{a\in\mathrm{A}\\ j,c\in\mathrm{B}}}\frac{2V_{pjac}V_{qjac}}{\omega+\varepsilon_j-\varepsilon_a-\varepsilon_c}, \tag{8b}$$

where

$$V_{ijkl}=\langle\varphi_i(1)\varphi_j(2)|1/r_{12}|\varphi_k(1)\varphi_l(2)\rangle. \tag{9}$$

In order to get the IPs, we need to find the poles of the G matrix in Eq. (1). Here we introduce the assumption,

$$G_{kk}^{-1}\gg G_{kl}^{-1} \quad (k\neq l). \tag{10}$$

The validity of this assumption has been discussed by Cederbaum [4] and for our examples we confirmed it from the numerical values. The introduction of this approximation simplifies the process of finding the poles of the G matrix. The G^{-1} matrix becomes a diagonal matrix and so the G matrix is also diagonal. From Eq. (4) the diagonal matrix element of G is

$$G_{kk}=\frac{1}{\omega-\varepsilon_k-\Sigma_{kk}}. \tag{11}$$

One pole of G is at

$$\omega(k)=\varepsilon_k+\Sigma_{kk} \tag{12}$$

and the vertical ionization potential from the orbital k is

$$\mathrm{IP}_k=-\omega(k)=-\varepsilon_k-\Sigma_{kk}. \tag{13}$$

So $-\Sigma_{kk}$ is the correction to Koopmans' theorem [5]. In particular the IP from the orbital k of atom A when influenced by atom B is the solution for ω of

$$\omega=-\varepsilon_k-\sum_{i,l,a\in \mathrm{A}}\frac{(2V_{kail}-V_{kali})V_{kail}}{\omega+\varepsilon_a-\varepsilon_i-\varepsilon_l}-\sum_{i,a,b\in \mathrm{A}}\frac{(2V_{kiab}-V_{kiba})V_{kiab}}{\omega+\varepsilon_i-\varepsilon_a-\varepsilon_b} \tag{14a}$$

$$-\sum_{\substack{i\in \mathrm{A}\\ j,c\in \mathrm{B}}}\frac{2(V_{kcij})^2}{\omega+\varepsilon_c-\varepsilon_i-\varepsilon_j}-\sum_{\substack{a\in \mathrm{A}\\ j,c\in \mathrm{B}}}\frac{2(V_{kjac})^2}{\omega+\varepsilon_j-\varepsilon_a-\varepsilon_c} \tag{14b}$$

and this can usually be estimated by approximating for ω by ε_k in the denominators so that

$$\mathrm{IP}_k^{\mathrm{A}}=-\varepsilon_k-\sum_{i,l,a\in \mathrm{A}}\frac{(2V_{kail}-V_{kali})V_{kail}}{\varepsilon_k+\varepsilon_a-\varepsilon_i-\varepsilon_l}+\sum_{i,a,b\in \mathrm{A}}\frac{(2V_{kiab}-V_{kiba})V_{kiab}}{\varepsilon_k+\varepsilon_i-\varepsilon_a-\varepsilon_b} \tag{14c}$$

$$-\sum_{\substack{i\in \mathrm{A}\\ j,c\in \mathrm{B}}}\frac{2(V_{kcij})^2}{\varepsilon_k+\varepsilon_c-\varepsilon_i-\varepsilon_j}-\sum_{\substack{a\in \mathrm{A}\\ j,c\in \mathrm{B}}}\frac{2(V_{kjac})^2}{\varepsilon_k+\varepsilon_j-\varepsilon_a-\varepsilon_c}. \tag{14d}$$

3. Physical interpretation of the IP

When only atom A exists, the IP from the orbital k of atom A is described by Eq. (14c). The first term is the IP according to Koopmans' theorem. The second and third terms are contributions from one electron and two electron excitation configurations. These terms show the effects of orbital relaxation after the ejection of an electron and of electron correlation inside the atom [6]. Equation (14d) gives the extra terms expressing the influence of atom B on atom A. If atom A and B are at a large separation, they interact through their Van der Waals interaction. Now if $|A\rangle_0$ and $|B\rangle_0$ are Slater determinants constructed from the Hartree-Fock atomic orbitals of A and B, respectively, the ground-state of the A and B system $|AB\rangle_0$ is described approximately as the product

$$|AB\rangle_0=|A\rangle_0|B\rangle_0. \tag{15}$$

The zero-th order total Hamiltonian of the A and B system, H_0^{AB}, satisfies

$$H_0^{\mathrm{AB}}|AB\rangle_0 = E_0|AB\rangle_0 \tag{16}$$

$$H_0^{\mathrm{AB}}|AB\rangle_K = E_K|AB\rangle_K, \tag{17}$$

where $|AB\rangle_K$ is an arbitrary excited state of the A and B system and E_0 and E_K are total energies of the ground-state and the excited state K of the system.

The interaction Hamiltonian between A and B is defined as

$$H_{\mathrm{int}}^{\mathrm{AB}} = -\sum_{n\in \mathrm{B}}^{N_{\mathrm{B}}} \frac{Z_{\mathrm{A}}}{r_{\mathrm{A}n}} - \sum_{m\in \mathrm{A}}^{N_{\mathrm{A}}} \frac{Z_{\mathrm{B}}}{r_{\mathrm{B}m}} + \sum_{m\in \mathrm{A}}^{N_{\mathrm{A}}} \sum_{n\in \mathrm{B}}^{N_{\mathrm{B}}} \frac{1}{r_{mn}} + \frac{Z_{\mathrm{A}}Z_{\mathrm{B}}}{R_{\mathrm{AB}}}, \tag{18}$$

where $Z_{\mathrm{A}}, Z_{\mathrm{B}}$ are nuclear charges and $N_{\mathrm{A}}, N_{\mathrm{B}}$ are the numbers of electrons of A, B, so using second order perturbation theory, their Van der Waals interaction energy is

$$E_{\mathrm{VdW}}^{\mathrm{AB}} = {}_0\langle AB|H_{\mathrm{int}}^{\mathrm{AB}}|AB\rangle_0 + \sum_{K\neq 0} \frac{{}_0\langle AB|H_{\mathrm{int}}^{\mathrm{AB}}|AB\rangle_K\, {}_K\langle AB|H_{\mathrm{int}}^{\mathrm{AB}}|AB\rangle_0}{E_0 - E_K} \tag{19}$$

and the first is zero because of the spherically symmetric electron distribution of each atom. By the use of Eq. (15) we can calculate the second term. One-electron excitation configurations in K do not contribute. From the contributions of the two-electron excitation configurations the Van der Waals interaction energy to second order is

$$E_{\mathrm{VdW}}^{\mathrm{AB}} = \sum_{\substack{i,a\in \mathrm{A}\\ j,c\in \mathrm{B}}} \frac{4(V_{ijac})^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_c}. \tag{20}$$

Next we think about the state of atom A after an electron has been ejected. We define A_k^+ as the cation of A which has a hole in orbital k. A long-range force acts between A_k^+ and atom B. The interaction Hamiltonian of the A_k^+ and B system is a little different from Eq. (18):

$$H_{\mathrm{long}}^{\mathrm{A}_k^+\mathrm{B}} = -\sum_{n\in \mathrm{B}}^{N_{\mathrm{B}}} \frac{Z_{\mathrm{A}}}{r_{\mathrm{A}n}} - \sum_{m\in \mathrm{A}}^{N_{\mathrm{A}}-1} \frac{Z_{\mathrm{B}}}{r_{\mathrm{B}m}} + \sum_{m\in \mathrm{A}}^{N_{\mathrm{A}}-1} \sum_{n\in \mathrm{B}}^{N_{\mathrm{B}}} \frac{1}{r_{mn}} + \frac{Z_{\mathrm{A}}Z_{\mathrm{B}}}{R_{\mathrm{AB}}}, \tag{21}$$

where $|\mathrm{A}_k^+\mathrm{B}\rangle_0 = |\mathrm{A}_k^+\rangle_0|\mathrm{B}\rangle_0$ as before. $|\mathrm{A}_k^+\rangle_0$ can be made from the same Hartree–Fock orbitals as for the neutral atom A. Hence, by the perturbation to second order, the long-range interaction energy is

$$E_{\mathrm{long}}^{\mathrm{A}_k^+\mathrm{B}} = \sum_{j,c\in \mathrm{B}} \frac{2(V_{kjkc})^2}{\varepsilon_k + \varepsilon_j - \varepsilon_k - \varepsilon_c} + \sum_{\substack{i,a\in \mathrm{A}\\ j,c\in \mathrm{B}}} \frac{4(V_{ijac})^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_c} \tag{22a}$$

$$- \sum_{\substack{a\in \mathrm{A}\\ j,c\in \mathrm{B}}} \frac{2(V_{kjac})^2}{\varepsilon_k + \varepsilon_j - \varepsilon_a - \varepsilon_c} + \sum_{\substack{i\in \mathrm{A}\\ j,c\in \mathrm{B}}}^{i\neq k} \frac{2(V_{ijkc})^2}{\varepsilon_i + \varepsilon_j - \varepsilon_k - \varepsilon_c}, \tag{22b}$$

where the first term is the contribution from the one-electron excitation configurations and the second to fourth terms are contributions from the two-electron excitation configurations. Now we define the ground-state energy of atom A and

B as E_A and E_B, and of the cation A_k^+ as E^+_{Ak}, then the IP from the orbital k of atom A in the A and B system is

$$\mathrm{IP}_k^A = (E^+_{Ak} + E_B + E^{A_k^+B}_{\mathrm{long}}) - (E_A + E_B + E^{AB}_{\mathrm{VdW}}) \tag{23a}$$

$$= (E^+_{Ak} - E_A + E^{A_k^+B}_{\mathrm{long}} - E^{AB}_{\mathrm{VdW}}) \tag{23b}$$

$$E^+_{Ak} - E_A = -\varepsilon_k + \Delta E_{\mathrm{relx}} + \Delta E_{\mathrm{corr}}, \tag{24}$$

where ΔE_{relx}, ΔE_{corr} are the orbital relaxation and electron correlation effects of the lone atom A ionization.

From Eqs. (20), (22a), (22b), (23b) and (24)

$$\mathrm{IP}_k^A = -\varepsilon_k + \Delta E_{\mathrm{relx}} + \Delta E_{\mathrm{corr}} \tag{25a}$$

$$+ \sum_{\substack{i\in A\\ j,c\in B}} \frac{2(V_{ijkc})^2}{\varepsilon_i + \varepsilon_j - \varepsilon_k - \varepsilon_c} - \sum_{\substack{a\in A\\ j,c\in B}} \frac{2(V_{kjac})^2}{\varepsilon_k + \varepsilon_j - \varepsilon_a - \varepsilon_c}. \tag{25b}$$

In Eqs. (14a) and (14b) we assumed that $\omega = \varepsilon_k$. This means that the truncation of the perturbation to second order and Eq. (14d) are equivalent to Eq. (25b). That is, it is shown that the equation of the IP, when one electron is ejected from atom A in the A and B system, involves terms which relate to the Van der Waals interaction between atoms A and B and the long-range interaction between cation A and atom B. In practice, for the calculation of the Van der Waals interaction energy it is known that a perturbation starting from the Hartree-Fock orbitals of each atom has slow convergency. Refinement of the zero-th order Hamiltonian has been proposed [8] and is used for the numerical calculations in Sect. 5.

4. Two hydrogen atoms

The simplest example consists of two hydrogen atoms at large separations. In general, Eqs. (14a)-(14d) are applicable only to the closed shell atom-closed shell atom interaction. It is exceptional that it can be used for the hydrogen-hydrogen interaction. But as shown later we require ROHF orbitals for the atomic orbitals of hydrogen and Eqs. (14a)-(14d) are valid for these orbitals. In this case, each atom has only one electron so there is no electron correlation in each atom and the second and third terms of Eq. (14c) do not exist. The IP from the $1s$ orbital of hydrogen atom A, by Eqs. (14c) and (14d), is

$$\mathrm{IP}_{1s}^A = -\varepsilon_{1s} + \sum_{c\in B} \frac{(V_{1s1s1sc})^2}{\varepsilon_{1s} + \varepsilon_{1s} - \varepsilon_{1s} - \varepsilon_c} - \sum_{\substack{a\in A\\ c\in B}} \frac{(V_{1s1sac})^2}{\varepsilon_{1s} + \varepsilon_{1s} - \varepsilon_a - \varepsilon_c}, \tag{26}$$

where the second and third terms have factor 1 because the orbitals are singly-occupied. If electron 1 belongs to A and 2 to B then the interaction potential between the two hydrogen atoms

$$H_{\mathrm{int}} = -\frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}} + \frac{1}{R_{AB}}. \tag{27}$$

Using the Hartree-Fock orbitals of each hydrogen atom we can get the Van der Waals interaction by the perturbation method.

$$E_{\mathrm{VdW}} = \sum_{\substack{a \in \mathrm{A} \\ c \in \mathrm{B}}} \frac{(V_{1s1sac})^2}{\varepsilon_{1s} + \varepsilon_{1s} - \varepsilon_a - \varepsilon_c}. \tag{28}$$

Next, the long-range interaction Hamiltonian between a proton (A) and a hydrogen atom (B) is

$$H_{\mathrm{long}} = -\frac{1}{r_{2\mathrm{A}}} + \frac{1}{R_{\mathrm{AB}}} \tag{29}$$

and the interaction energy is

$$E_{\mathrm{long}} = \sum_{c \in \mathrm{B}} \frac{\langle \varphi_{1s}(2) | 1/r_{2\mathrm{A}} | \varphi_c(2) \rangle^2}{\varepsilon_{1s} - \varepsilon_c} = \sum_{c \in \mathrm{B}} \frac{(V_{1s1s1sc})^2}{\varepsilon_{1s} + \varepsilon_{1s} - \varepsilon_{1s} - \varepsilon_c}, \tag{30}$$

where the second equality is due to the spherical symmetry of the 1*s* orbital of atom A.

Thus Eq. (26) can be described as

$$\mathrm{IP}_{1s}^{\mathrm{A}} = -\varepsilon_{1s} + E_{\mathrm{long}} - E_{\mathrm{VdW}}. \tag{31}$$

Before ionization, the total energy of this system is

$$E_{\mathrm{AB}} = 2\varepsilon_{1s} + E_{\mathrm{VdW}}. \tag{32}$$

After the ejection of an electron, the total energy is

$$E_{\mathrm{AB}}^{+} = \varepsilon_{1s} + E_{\mathrm{long}}. \tag{33}$$

So the IP is

$$\mathrm{IP}_{1s}^{\mathrm{A}} = E_{\mathrm{AB}}^{+} - E_{\mathrm{AB}} = -\varepsilon_{1s} + E_{\mathrm{long}} - E_{\mathrm{VdW}}. \tag{34}$$

This is equivalent to Eq. (31) and shows the energy conservation law in the ionization process.

We have performed calculations on the IP of two hydrogen atoms at large separations. We used the program IMSPAK [9] for the calculations of the atomic orbitals of the lone hydrogen atom and two-electron integrals of the basis set. The atomic orbitals of hydrogen were found by Davidson's ROHF routine in IMSPAK [9, 10]. Huzinaga's [10*s*6*p*] primitive basis set [11] was used for each hydrogen atom. The first term of Eq. (26) is the orbital energy of the 1*s* orbital of the hydrogen atom and was −0.4999986 hartree. This is very close to the exact one, −0.5 hartree. If we know the atomic orbital coefficients and two-electron integrals over the basis set, we can calculate the second and third terms of Eq. (26). We performed the calculations at the separations of 5, 10, 15, 20 bohr. The results are shown in Table 1. Usually long-range interactions between an ion and an atom are expanded as

$$E_{\mathrm{long}} = -\frac{C_4}{R^4} - \frac{C_6^{+}}{R^6} - \frac{C_8^{+}}{R^8} \cdots \tag{35}$$

Table 1. Long-range and Van der Waals interactions (in hartree) of two hydrogen atoms at various separations[a]

R	5	10	15	20
E_{Long}	$-3.28307E-3$	$-2.24952E-4$	$-4.44409E-5$	$-1.40615E-5$
C_4	2.05192[b]	2.24952[b]	2.24982[b]	2.24984[b]
%	91.1964[b]	99.9787[b]	99.9920[b]	99.9929[b]
E_{VdW}	$-3.12686E-4$	$-6.48846E-6$	$-5.70433E-7$	$-1.01505E-7$
C_6	4.88572[c]	6.48846[c]	6.49759[c]	6.49632[c]
%	75.1762[c]	99.8374[c]	99.9779[c]	99.9584[c]
IP	0.497028	0.499780	0.499955	0.499985
$\lvert\Delta \mathrm{IP}\rvert$	$2.97038E-3$	$2.18464E-4$	$4.38705E-5$	$1.39600E-5$

[a] Unit of distance is bohr. Basis set is [10*s*6*p*]
[b] C_4 is the first one in Eq. (35). $\% = (C_4/2.25) \times 100$
[c] C_6 is the first one in Eq. (36). $\% = (C_6/6.499026) \times 100$

and Van der Waals interactions between atoms as

$$E_{\mathrm{VdW}} = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R_{10}} \cdots, \tag{36}$$

where R is distance between nuclei.

Reliable values for C_4 and C_6 are known. For example, Koga et al. [12] have obtained ($C_4 = 2.25$, $C_6 = 6.499026705 \cdots$). In Table 1 at 15 bohr and 20 bohr our results, for C_4, are 99.99% and, for C_6, 99.9% of Koga's ones. We can see that the agreement is very close. The result at 10 bohr shows signs of the breakdown of Van der Waals interaction energy caused by the generation of chemical bonding to form the H_2 molecule. Similarly, the charge in the cation delocalizes to form H_2^+. At 5 bohr, these effects become more notable. We also performed the same calculation using a different basis set. We used Dunning's [4*s*/2*s*] for the *s* orbitals [13] and Huzinaga's [5*p*] for the *p* orbitals. The results are in Table 2.

Table 2. Long-range and Van der Waals interactions (in hartree) of two hydrogen atoms at various separations[a]

R	5	10	15	20
E_{Long}	$-2.88366E-3$	$-1.87304E-4$	$-3.69982E-5$	$-1.17065E-5$
C_4	1.80229[b]	1.87304[b]	1.87303[b]	1.87304[b]
%	80.1018[b]	83.2462[b]	83.2458[b]	83.2462[b]
E_{VdW}	$-2.56257E-4$	$-4.80824E-6$	$-4.22133E-7$	$-7.51301E-7$
C_6	4.00402[c]	4.80824[c]	4.80836[c]	4.80833[c]
%	61.6095[c]	73.9840[c]	73.9858[c]	73.9854[c]

[a] Unit of distance is bohr. Basis set is [2*s*5*p*]
[b] C_4 is the first one in Eq. (35). $\% = (C_4/2.25) \times 100$
[c] C_6 is the first one in Eq. (36). $\% = (C_6/6.499026) \times 100$

This time we got 83.24% for C_4 and 73.98% for C_6 compared with Koga's results. These are far from satisfactory. We may conclude that the accuracy of the electron distributions of the ground-state as well as of the excited state plays an important role in the precise calculations of Van der Waals and long-range interactions.

We also performed full CI calculations on the two hydrogen atoms system putting Huzinaga's [10*s*6*p*] primitive basis set on each atom and using the program MELD [14]. The results are in Table 3. Beyond 15 bohr, we got Van der Waals interaction energies of $-0.6E-6$ hartree for 15 bohr, and of $-0.1E-6$ hartree for 20 bohr. These are 91.2% and 93.5% of the results from Eq. (36). We found that a full CI calculation on the two hydrogen atoms system with a large enough basis set could show relatively good Van der Waals interaction energies. The hydrogen atom and proton system has only one electron and there is no electron correlation. By UHF calculations we got the long-range interaction energy in this system. We got 106% for 15 bohr and 99.3% for 20 bohr compared with the values from Eq. (35). We define ΔIP as the difference between the IP and the orbital energy. ΔIPs are also shown in Table 3. Correspondence with the Green's function's results is good for the 15, 20 bohr cases. But it is obvious that our method is superior to the CI method in terms of both accuracy and cost, if the reference state of the CI uses the RHF molecular orbitals of H_2.

In Table 3 the upper figure in the second row shows the total energy with two electrons in the singlet state and the lower figure in the triplet state. It seems that the potential energy curves of the singlet and the triplet will meet at a point where the distance of two hydrogen atoms is a little larger than 10 bohr. Beyond this point, energy degeneracy occurs and the energies of singlet and triplet states become the same. In this region, we may see that chemical bonding has disappeared and only the Van der Waals forces remain. This is consistent with our

Table 3. Full CI calculations of two hydrogen atoms systems (in hartree)[a]

R	5	10	15	20
H-H	$S-1.0034900$	-1.0000044		
Total Energy	$T-0.9985760$	-1.0000034	-0.9999978	-0.9999973
E_{VdW}			$-6.0E-7$	$-1.0E-7$
E_{VdW} from Eq. (36)			$-6.58E-7$	$-1.07E-7$
%			91.2	93.5
$H\text{-}H^+$				
Total Energy	-0.5240664	-0.5005611	-0.5000466	-0.5000127
E_{Long}			$-4.8E-5$	$-1.41E-5$
E_{Long} from Eq. (35)			$-4.51E-5$	$-1.42E-5$
%			106	99.3
IP	0.479424	0.499443	0.4999512	0.4999846
$\lvert\Delta \mathrm{IP}\rvert$	$2.0575E-2$	$5.553E-4$	$4.74E-5$	$1.40E-5$

[a] Unit of distance is bohr. Basis set is [10*s*6*p*]. 1*s* orbital energy is -0.4999986 hartree

results on Van der Waals interaction energies which experience breakdown below 10 bohr.

For the IP of molecules, Gregson and Hall [15] suggested a correction formula to the Koopmans' theorem based on classical electrostatics. They discussed how the charge-induced dipole interactions within the cation influenced the IP. Their calculations of the IPs of the chloro-ethylenes are in good agreement with experiment. In the present work we can see the same inter-atom dipole effect on the IP. It is this term which stabilizes the localized charge on one atom when the separations are large. Thus, when the triplet state wavefunction is written using atomic orbitals, it is adapted to the charge distribution of the cation and ionization follows the atomic Koopmans' theorem rather than the molecular one. Since the atomic orbital can be regarded as the superposition of the symmetric and antisymmetric orbitals of H_2, the resulting spectral intensities of these will be approximately 0.5. At smaller separations, when exchange terms begin to be appreciable, the charge is distributed, as Koopmans' theorem indicates, according to the molecular orbital. In general [2] Koopmans' theorem is a good approximation for valence electrons at equilibrium geometries but this example shows that at large separations it breaks down even for valence electrons.

5. Two helium atoms

Next we think about the system of two helium atoms, A and B, at large separations. The IP of the 1s orbital of atom A polarized by atom B is written, using Eqs. (14c) and (14d).

$$\mathrm{IP}_{1s}^{\mathrm{A}} = -\varepsilon_{1s} - \sum_{a\in \mathrm{A}} \frac{(2V_{1sa1s1s} - V_{1sa1s1s})V_{1sa1s1s}}{\varepsilon_{1s} + \varepsilon_a - \varepsilon_{1s} - \varepsilon_{1s}} - \sum_{a,b\in \mathrm{A}} \frac{(2V_{1s1sab} - V_{1s1sba})V_{1s1sab}}{\varepsilon_{1s} + \varepsilon_{1s} - \varepsilon_a - \varepsilon_b} \tag{37a}$$

$$- \sum_{c\in \mathrm{B}} \frac{2(V_{1sc1s1s})^2}{\varepsilon_{1s} + \varepsilon_c - \varepsilon_{1s} - \varepsilon_{1s}} - \sum_{\substack{a\in \mathrm{A}\\ c\in \mathrm{B}}} \frac{2(V_{1s1sac})^2}{\varepsilon_{1s} + \varepsilon_{1s} - \varepsilon_a - \varepsilon_c}. \tag{37b}$$

We can divide this into two parts, first the terms relating to atom A only, viz the three terms in Eq (37a), and then the remaining terms in Eq. (37b) to both atom A and atom B. The first term of Eq. (37a) is the energy of the 1s orbital of helium atom A and the second and third terms are relaxation and electron correlation effects for the atomic IP. We calculated this IP by the same method as in the previous section except that the orbitals are now doubly-occupied. Again, the use of atomic orbitals implies that the cation has all its charge on one atom. It is convenient to consider first a single helium atom and our results on this are compared with those from various other methods in Table 4. Compared with the experimental value, the IP from the Green's function is as reliable as that from the full CI. Next we consider two helium atoms and evaluate the terms of Eq. (37b), related to the Van der Waals and long-range interactions. Calculated results on these are shown in Table 5. Davison has obtained reliable C_4 and C_6 coefficients for helium atoms. ($C_4 = 0.692$, $C_6 = 1.47$) [18]. We have obtained, for C_4, 72%

Table 4. IP of helium atom by various methods (in eV)

Full CI[a]	24.490
Green's function[b]	24.463
Koopmans' theorem[c]	24.979
ΔSCF[d]	23.448
Experiment	24.587

[a] Basis set is [10*s*6*p*]
[b] Basis set is [10*s*6*p*]
[c] [16]
[d] [17]

and, for C_6, 76% of Davison's results and these are not very satisfactory. It is well-known that the convergence of the perturbation expansion is slow when Van der Waals interactions are calculated by using products of each atom's Hartree-Fock wavefunctions as zero-th order wavefunctions. We think our poor results are due to this reason. A refinement of the zero-th order Hamiltonian has been discussed by Fröman and Hall [7] and developed as the ICSCF method by Davidson [8]. We can write down the ICSCF Hamiltonian as

$$H = H'_0 + H'_l \tag{38}$$

$$H'_0 = H^{\mathrm{HF}}_{\mathrm{A}} + H^{\mathrm{HF}}_{\mathrm{B}} + (1-P_{\mathrm{A}})\alpha_{\mathrm{A}}(1-P_{\mathrm{A}}) + (1-P_{\mathrm{B}})\alpha_{\mathrm{B}}(1-P_{\mathrm{B}}) \tag{39}$$

$$H'_l = H^{\mathrm{correl}}_{\mathrm{A}} + H^{\mathrm{correl}}_{\mathrm{B}} + H_{\mathrm{AB}} - (1-P_{\mathrm{A}})\alpha_{\mathrm{A}}(1-P_{\mathrm{A}}) - (1-P_{\mathrm{B}})\alpha_{\mathrm{B}}(1-P_{\mathrm{B}}), \tag{40}$$

where P_{A} is the projection operator

$$P_{\mathrm{A}} = \sum_{\substack{i \in \mathrm{A} \\ i = \mathrm{occ}}} |\varphi_i\rangle\langle\varphi_i| \tag{41}$$

Table 5. Long-range and Van der Waals interactions (in hartree) of two helium atoms at various separations[a]

R	5	10	15	20
E_{Long}	$-7.93302E-4$	$-4.98302E-5$	$-9.84302E-6$	$-3.11436E-6$
C_4	0.495814	0.498302	0.498303	0.498298
%	71.6494[b]	72.0090[b]	72.0091[b]	72.0084[b]
E_{VdW}	$-6.93728E-5$[d]	$-1.11670E-6$[d]	$-9.80160E-8$[d]	$-1.74466E-8$[d]
C_6	1.08395	1.11670	1.11646	1.11658
%	73.7381[c]	75.9660[c]	75.9497[c]	75.9578[c]
IP	0.896012	0.898764	0.898938	0.898968
|ΔIP|	$2.97038E-3$	$2.18464E-4$	$4.38705E-5$	$1.39600E-5$

[a] Unit of distance is bohr. Basis set is [10*s*6*p*]. IP of helium atom is −0.8989823 hartree
[b] $\% = (C_4/0.692) \times 100$
[c] $\% = (C_6/1.47) \times 100$
[d] These are twice the second term of Eq. (37b)

and

$$\langle \varphi_a | \alpha_{\mathrm{A}} | \varphi_a \rangle = -J_{ia} + 2K_{ia} \tag{42}$$

$$J_{ia} = \langle \varphi_i(1)\varphi_a(2) | 1/r_{12} | \varphi_i(1)\varphi_a(2) \rangle \tag{43}$$

$$K_{ia} = \langle \varphi_i(1)\varphi_a(2) | 1/r_{12} | \varphi_a(1)\varphi_i(2) \rangle . \tag{44}$$

We can expand the Green's function using this Hamiltonian. The first order self-energy is zero as in Sect. 2. The second order self-energy suffers some changes and, for the helium atoms, is

$$\Sigma_{pq}^{(2)}(\omega) = \sum_{a \in \mathrm{A}} \frac{(2V_{pa1s1s} - V_{pa1s1s})V_{qa1s1s}}{\omega + \varepsilon_a - \varepsilon_{1s} - \varepsilon_{1s} - J_{1sa} + 2K_{1sa}} \tag{45a}$$

$$+ \sum_{a,b \in \mathrm{A}} \frac{(2V_{p1sab} - V_{p1sba})V_{q1sab}}{\omega + \varepsilon_{1s} - \varepsilon_a - \varepsilon_b + J_{1sa} + J_{1sb} - 2K_{1sa} - SK_{1sb}} \tag{45b}$$

$$+ \sum_{c \in \mathrm{B}} \frac{2V_{pc1s1s}V_{qc1s1s}}{\omega + \varepsilon_c - \varepsilon_{1s} - \varepsilon_{1s} - J_{1sc} + 2K_{1sc}} \tag{45c}$$

$$+ \sum_{\substack{a \in \mathrm{A} \\ c \in \mathrm{B}}} \frac{2V_{p1sac}V_{q1sac}}{\omega + \varepsilon_{1s} - \varepsilon_a - \varepsilon_c + J_{1sa} + J_{1sc} - 2K_{1sa} - 2K_{1sc}} . \tag{45d}$$

Compared with Eqs. (37a) and (37b) the denominators of Eqs. (45a)-(45d) have the extra terms, J_{ia} and K_{ia}. Substituting ε_{1s} for ω we get the refined interaction energies shown in Table 6. We now have, for C_4, 90% and, for C_6, 95% of Davison's results. This confirms that the Hamiltonian of Eq. (38) is superior to the conventional one for the calculation of inter-atomic energies. It also shows that the charge on the ion remains localized on one atom even at a separation of 5 bohr.

We performed SD-CI calculations for two helium atoms and for a helium atom and a helium cation at large separations. The results are in Table 7. In this case

Table 6. Long-range and Van der Waals interactions (in hartree) of two helium atoms at various separations[a]

R	5	10	15	20
E_{Long}	$-9.94214E-4$	$-6.24176E-5$	$-1.23294E-5$	$-3.90108E-6$
C_4	0.621384	0.624176	0.624176	0.624173
%	89.7954[b]	90.1988[b]	90.1988[b]	90.1984[b]
E_{VdW}	$-8.68376E-5$[d]	$-1.39625E-6$[d]	$-1.22554E-7$[d]	$-2.18147E-8$[d]
C_6	1.35684	1.39625	1.39597	1.39614
%	92.3020[c]	94.9830[c]	94.9639[c]	94.9755[c]
$\|\Delta\mathrm{IP}\|$	$9.50795E-4$	$6.17195E-5$	$1.22981E-5$	$3.89017E-6$

[a] The ICSCF Hamiltonian is used. Unit of distance is bohr. Basis set is [10*s*6*p*]

[b] $\% = (C_4/0.692) \times 100$

[c] $\% = (C_6/1.47) \times 100$

[d] These are twice of Eq. (45d)

Table 7. SD-CI calculations of two helium atoms systems (in hartree)[a]

R	5	10	15	20
He-He				
Total Energy	−5.7988659	−5.7989130	−5.7989115	−5.7989113
He-He$^+$				
Total Energy	−4.9052529	−4.8991871	−4.8991224	−4.8991129
IP	0.8936130	0.8997259	0.8997891	0.8997984
$\|\Delta \text{IP}\|$	$6.35760E-3$	$2.44701E-4$	$1.81501E-4$	$1.72201E-4$

[a] Unit of distance is bohr. Basis set is [10*s*6*p*]. IP of helium atom is −0.8999706 hartree

we did not get good values for either the Van der Waals interaction energy or the long-range interaction energy. This is because the SD-CI method is not accurate enough to calculate such sensitive energies and this CI method has the defect of the size-inconsistency.

6. IP of weakly-interacting Van der Waals molecules

The examples considered in Sects. 4 and 5 are difficult to relate to experiment. By contrast, Pratt et al. have recently succeeded in measuring experimentally the IP of weakly-interacting Van der Waals molecules (NeAr, NeKr, NeXe) [19]. The physical interpretation of the IP discussed in Sects. 2 and 3 can be adapted to these systems. Since these are heteromolecules there is no problem due to molecular bonding or charge delocalization as arose in the homomolecules. Unfortunately, a change of equilibrium structure occurs when an electron is ejected and the IP involves effects of structure relaxation. In this case we cannot describe a cationic system by orbitals of the neutral system in its equilibrium configuration and an orbital perturbation description which focuses on the orbital whence an electron is ejected will break down. We need then to consider the Van der Waals and long-range interactions of the whole system at different separations and also the zero point vibrational energies.

One of the main interests is to know the equilibrium internuclear distance of neutral (R_n) and cationic (R_c) systems. The R_n for NeAr, NeXe, NeKr have been determined by experiment [20]. But the R_c for these molecules have not yet been determined experimentally. Pratt et al. have estimated R_c by using IP. They have regarded the long-range interaction as only C_4/R_c^4. ($C_4 = \alpha_p/2$; α_p is the polarizability of Ne atom). But we have found that C_6^+/R_c^6 is not negligible. We have followed Pratt's method of calculating R_c but included the E_6^c term. Following Siska [25] we define $C_6^+ = C_6 + \alpha_q/2$, where C_6 is the dispersion constant of the neutral Ne X(X = Ar, Kr, Xe) molecule and α_q is the quadrupole polarizability of the Ne atom.

Thus, the long-range interaction energy of the cationic system is written as

$$E_{\text{long}} = E_4^C + E_6^C = \frac{C_4}{R_c^4} + \frac{C_6^+}{R_c^6}. \tag{46}$$

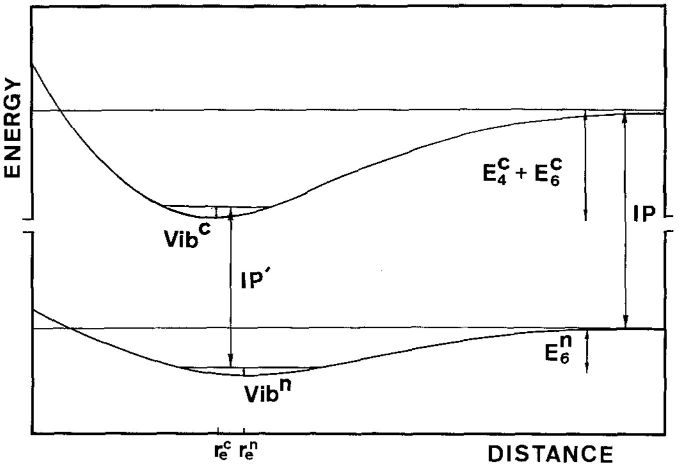

Fig. 1. Potential energy profile and ionization process of Ne X (X = Ar, Kr, Xe)

Table 8. Constants and results for the potential energy profile of rare-gas Van der Waals molecules[a]

	NeAr	NeKr	NeXe
R_e^n	6.482[b]	6.765[b]	7.087[b]
C_6	556 889[c]	775 102[c]	1 125 626[c]
C_6^+	644 838[c,d]	863 051[c,d]	1 213 575[c,d]
C_4	36 267[e]	36 267[e]	36 267[e]
E_6^n	7.510	8.085	8.960
Vib^n	1.75[f]	1.62[f]	1.62[f]
Vib^c	6.10[g]	4.90[g]	4.20[g]
$\|\Delta IP\|$	74.70[h]	49.70[h]	36.00[h]
E_4^c	51.78	35.09	25.25
E_6^c	34.78	25.98	22.29
R_e^c (this work)	5.145	5.670	6.156
R_e^c (Pratt, Dehmer)	4.62[i]	5.06[i]	5.45[i]
R_e^c (Hausamann, Morgner)	5.25[j]	5.75[j]	6.50[j]

[a] Unit of energy is meV, distance is bohr
[b] [20]
[c] [20]
[d] [22]
[e] [21]
[f] [23]
[g] [24]
[h] [19]
[i] [19]
[j] [24]

The potential energy profile and the IP are shown in Fig. 1. From this

$$\Delta \mathrm{IP} = \mathrm{IP} - \mathrm{IP}' = E_4^c + E_6^c - E_6^n + Vib^n - Vib^c, \tag{47}$$

where E_6^n is the Van der Waals interaction energy between neutral atoms. E_6^c and E_4^c are long-range interaction energies of the cationic system. Vib^n and Vib^c are the zero-point vibrational energies of the neutral and cationic molecules. We have estimated R_c using published data; ΔIP from [19], R_n and C_6 from [20], α_p from [21], α_q from [22], Vib^n from [23], Vib^c from [24]. In Table 8 we compare our results with the others'. Hausamann et al. [24] have made a good estimate of the potential energy curves by fitting the spectroscopy data. Our results are closer to Hausamann's than Pratt's. We conclude that it is necessary to consider E_6^c to estimate R_c. These examples clearly show that the IP of a weakly-interacting Van der Waals molecule involves the Van der Waals and the long-range interactions in it, as is discussed in Sects. 2 and 3.

7. Summary

We have derived an IP formula for systems which have two atoms at large separations by a Green's function method. The correction terms to the atomic Koopmans' theorem formula involve not only electron correlation and orbital relaxation terms in an atom but also Van der Waals and long-range interactions between atoms. Calculations were performed for interacting pairs of hydrogen atoms and helium atoms at large separations. For hydrogen atoms, we got very reliable results. We also showed that our ideas can be applied to the IPs of weakly-interacting rare-gas Van der Waals molecules.

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