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g-Hartree *ab initio* calculations of the ionization energies of the four-electron isoelectronic series

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The ionization energies of the four-electron isoelectronic series are calculated by both *g*-Hartree and Dirac-Hartree-Fock Rayleigh-Schrödinger (Møller-Plesset) second-order perturbation theory.

I. INTRODUCTION

During the last decade many efforts have been made in the development of theoretical approaches for the calculations of the ionization energies and the intensities.[1-6] By the configuration-interaction (CI) method one expands the fixed one-particle basis sets in terms of a large number of configurations. By the Rayleigh-Schrödinger perturbation theory (RSPT), the RS series for the total energy of the $(N-1)$-electron system is obtained employing a Hartree-Fock (HF) function in zeroth order comprised of $N-1$ canonical Fock orbitals from the N-electron system. The ionization potential can be obtained from the difference of the RSPT series of the total energies of N- and $(N-1)$-electron systems. By the diagrammatic techniques the terms in the RSPT series of the neutral and ionic total energies and their differences are conveniently determined employing operators in normal form and appropriate distinct Hugenholtz diagrams,[7,8] with subsequent vertex expansion to obtain the corresponding Goldstone energy diagrams in each order.

By the so-called quasiparticle Green's-function method, one obtains the ionization energy and intensity as the pole and its residue of the one-particle Green's function. Although these two methods are apparently different in spirit and outward appearance, when a Fock basis is employed, it is proved that these two methods are equivalent up to the third order and differ in the fourth and higher orders of perturbation theory.[9] The RSPT and Green's-function results differ in second and third order only by the effects of iteration in the solution of eigenvalue problem when the quasiparticle approximation is used as the starting value for the self-energy.

The *g*-Hartree method is a mean-field method which was derived exactly from the full relativistic QED action by using the functional method and expanding the grand-canonical partition function around the stationary point (which is given by the solution of the *g*-Hartree equation).[10] The method was extended so that electron energy level in this mean field, i.e., the eigenvalues of the *g*-Hartree equation are equal to the theoretically exact ionization energies.[11] It is shown that the numerical results by the *g*-Hartree method for the ionization energy give a good agreement with the experiment.[11-13]

So far much attention has been paid to the study of the single excitations from the neutral atoms and molecules. However, less attention has been paid to the study of single-hole excitations from the ionized atoms or molecules. In the ionized atoms, in comparison to the neutral atoms, the relaxation energy shift will be reduced very much because of absence of the intershell relaxation due to the outershell (valence) electrons which is often very dominating. However, the relaxation shift of an arbitrary electronic configuration will be relatively insensitive to an increase of the nuclear charge Z because of a balance between the Coulomb integrals becoming larger and the polarizability smaller for a given shell as Z increases. It would be very important to be able to calculate accurately the ionization energies of the ionized atoms. With an increase of Z the relativistic effects like the Breit interaction, vacuum polarization, self-energy, and QED corrections must also be taken into account.

In the present work I would like to calculate the ionization energy of the four-electron isoelectronic series ($Z=4$, 6, 8, and 10) by the *g*-Hartree (*g*-H) and Dirac-Hartree-Fock (DHF) Rayleigh-Schrödinger (RS) second-order perturbation theories in order to study the effects of the increase of nuclear charge on the correlation and relaxation of a single hole created in the ionized atoms.

II. THEORY

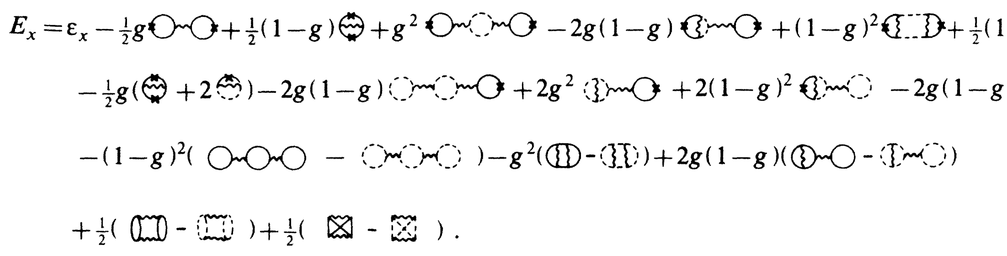
Pickup and Goscinski[14] derived the single-hole-ionization energy by using the Hartree-Fock-Rayleigh-Schrödinger perturbation theory (HFRSPT). One starts by dividing the full electronic Hamiltonian of the atomic system into a central-field part which describes N electrons moving in the field of the nucleus and an average central field due to the electrons and a perturbation. Introducing the Fock operator for the $(N-1)$-electron system, expanding the eigenfunctions and eigenvalues of the $N-1$ electron system about the corresponding ones of the N-electron system, we approximate the total energy of the $(N-1)$-electron system. Then we take a difference of the total energy of the N- and $(N-1)$-electron system and obtain the following expression as the ionization energy within the DHFRS second-order PT (DHFRS2PT):

$$E_x = \varepsilon_x + \sum_{j,a} \frac{|\langle xj\|xa\rangle|^2}{\varepsilon_a - \varepsilon_j} + \sum_{\substack{j\,(\neq x),\\ a,b}} \frac{|\langle xj\|ab\rangle|^2}{\varepsilon_x + \varepsilon_j - \varepsilon_a - \varepsilon_b} + \sum_{\substack{i,j(\neq x),\\ a}} \frac{|\langle xa\|ij\rangle|^2}{\varepsilon_x + \varepsilon_a - \varepsilon_i - \varepsilon_j} . \tag{1}$$

Here ε_x is the eigenvalue (Koopmans's energy) of the HF equation for the N-electron Hamiltonian. The second term is the nonhole hopping relaxation (predominately so-called monopole relaxation) term which describes the relaxation within the SCF picture. The third and fourth terms are the ground-state correlation and the hole-hopping relaxation (predominately dipole relaxation), respectively. One can also rewrite Eq. (1) in terms of the correlation and relaxation.

$$E_x=\varepsilon_x+\sum_{j,a,b}\frac{|\langle xj\|ab\rangle|^2}{\varepsilon_x+\varepsilon_j-\varepsilon_a-\varepsilon_b}+\sum_{\substack{i,j\\a}}\frac{|\langle xa\|ij\rangle|^2}{\varepsilon_x+\varepsilon_a-\varepsilon_i-\varepsilon_j}\ . \tag{2}$$

In the case of the g-Hartree method we start with the Møller-Plesset partitioning of the g-Hartree Hamiltonian. We introduce the g-Hartree potential as a central-field potential and use RSPT as in the case of DHFRS2PT.[15] We obtain the following diagrammatic expansions for the g-H second-order PT (g-H2PT):



(3)

Here the crossing is the propagator of the hole which is created by the initial core-hole excitation. The solid lines correspond to the electron propagators for the N and $N-1$ electron configurations. In Eq. (3) ε_x is the eigenvalue of the g-Hartree equation for the N electron system. The second to sixth terms are from the zeroth-order self-consistent-field (SCF) approximation. The second and third terms are the hole-hole self-interaction corrections and the fourth to sixth terms are nonhole hopping (SCF) relaxation terms. The seventh to fourteenth are from the first-order corrections. The seventh to the tenth terms correspond to the hole-hole self-interaction. The eleventh to fourteenth terms describe the interaction between the hole and the surrounding electrons. The fifteenth to last terms are from the second-order corrections. The last two terms are same as in the case of HFRS2PT.

We optimize so that the correlation and relaxation terms vanish and the eigenvalue becomes equal to the ionization energy,[11-13]

$$\Delta_x^{\text{corr}+\text{rel}}(g_0)=0,\Longrightarrow E_x=\varepsilon_x(g_0)\ . \tag{4}$$

Both occupied and unoccupied (discrete and continuum) orbitals are calculated numerically within the frozen-core approximation. The orbitals are generated by the frozen core g-H and DHF neutral ground-state potential of the initial-state electron configuration. The orbitals are calculated by using the new g-H and DHF codes modified from the DHF code provided by Johnson.[16] The new computer code for the numerical evaluation of the DHFRS2PT and g-H2PT series was written by the author[17] for the present work.

III. RESULTS AND DISCUSSIONS

In Tables I and II we summarize the results by the DHFRS theory and experimental data for the 1s and 2s levels of the four-electron isoelectronic series. The experimental data are taken from Bashkin and Stoner.[18] We list also the HFRS second- and third-order results by Hernandez and Langhoff.[19] They are calculated by using the finite basis sets of 6s,5p,2d Slater type orbitals which provide approximately 85% of the total correlation energies by the third-order HFRS calculations.

Note that the present fully relativistic numerical DHFRS2PT results are in excellent agreement with the HFRS2PT results using the finite-basis-sets method. However, one should note that the latter results are nonrelativistic results and the relativistic effects like the Breit interaction, vacuum polarization, self-energy, and QED corrections are neglected. In the present work these relativistic effects are obtained by the lowest-order approximation by using DHF code by Grant.[20] They are evaluated by the DHFΔSCF calculations. For the inner-shell 1s level the energy shifts are 0.03 eV for $Z=4$, 0.08 eV for $Z=6$, 0.22 eV for $Z=8$, and 0.45 eV for $Z=10$. The energy shift for the 2s level is negligible. The relativistic energy shift of the eigenvalue is -0.02 eV for the 1s level and negligible for the 2s level of the neutral Be($Z=4$). Even when we take these relativistic energy shifts into

TABLE I. Theoretical and experimental ionization energy of 1s core hole of the four-electron isoelectronic series (eV).

Z	Koopmans's energy	Δ SCF	DHFRS (second order)	HFRS (second order)	HFRS (third order)	Expt.
4	−128.8	−123.3	−124.9	−124.9	−123.9	−123.6
6	−344.4	−339.4	−340.6	−340.6	−340.0	
8	−669.7	−664.7	−665.7	−665.6	−665.0	
10	−1104.4	−1099.3	−1100.1			

TABLE II. Theoretical and experimental ionization energy of 2*s* core hole of the four-electron isoelectronic series (eV).

Z	Koopmans's energy	Δ SCF	DHFRS (second order)	HFRS (second order)	HFRS (third order)	Expt.
4	−8.42	−8.04	−8.9	−8.9	−9.1	−9.323
6	−46.1	−45.8	−47.1	−47.1	−47.5	−47.63
8	−111.4	−111.1	−112.8	−112.7	−113.2	−113.77
10	−204.1	−203.8	−205.8			−207.25

consideration, the agreement between the present fully numerical results and the finite-basis-sets results is good. When the discrepancy between the numerical results and finite-basis-sets results becomes non-negligible, the differences are most likely due to the level shifts which one obtains by coupling of the initial single hole with the degenerate or nearly degenerate Auger continua. When the finite basis sets are not good enough, the effects by the interaction between the initial single-hole state and continua states cannot be included properly. Conventional L^2 basis-set calculations of the shifts in RSPT are not expected to converge in these cases.[19]

The difference between the Koopmans energy and the DHFΔSCF result is interpreted as the nonhole hopping relaxation energy shift (predominantly monopole relaxation shift) which is fairly independent of an increase of nuclear charge Z. The relaxation effects are fairly independent of Z. The relaxation depends on a balance between the Coulomb integrals becoming larger and the polarizability smaller for a given shell as Z increases. The difference between the Koopmans's energy and the SCF energy is much more significant for the inner-shell ionization than for the outer-shell ionization. According to the Manne-Åberg sum rule,[21] within the HFΔSCF model, the Koopmans's energy corresponds to the average ionization energy. The difference between the average ionization energy and the main ionic ionization energy (which is approximately given by the ΔSCF energy) is small because of smaller probability for excitation states (normal and conjugate shake up, etc.) at outer ionization in the SCF model. The relaxation energy (the difference between the Koopmans's energy and the HFΔSCF energy) is reduced very much because of absence of outer-shell electrons. In the case of $Z=10$ the relaxation energy shift for the 1*s* and 2*s* levels of neutral neon is 23.78 and 3.24 eV, respectively. However, in the case of four-electron isoelectronic series, at $Z=10$ the relaxation energy shift is reduced to 5.1 and 0.3 eV, respectively. This is in accord with the observation that the relaxation of the inner shell is negligible and the intrashell relaxation is small compared to the intershell relaxation from the outer shells in a closed-shell ion.

The difference between the ΔSCF energy and the DHFRS2PT energy can be interpreted as a sum of the ground-state correlation-energy shift and the hole-hopping relaxation energy shift. The latter can be very important when the initial core hole can hop to the subshell where the angular momentum differs [(super) Coster-Kronig processes].[5,6] In the present case as only *s* orbitals are involved as the occupied orbitals of the initial state, the contribution from the hole-hopping relaxation processes is small and fairly independent of Z. The dominating part of the difference is from the ground-state correlation (GSC) energy shift which with an increase of Z decreases approximately in linear in the case of a 1*s* level and increases in the case of a 2*s* level. However, the total sum of the GSC energy shift increases gradually with an increase of Z. This is in accord with the observation that the total correlation energy calculated by the DHFRS2PT for the four-electron isoelectronic series increases gradually with an increase of Z.[22] In contrast to the relaxation energy shift, the GSC energy shift is relatively independent of the hole level considered. The magnitude of $1s^2$ and $2s^2$ pair correlation energy is of same order for the neutral atom Be. For the GSC of the four-electron isoelectronic series where only S orbitals are considered, the intershell interaction is much less important than the intrashell interaction.

In general, the third-order terms improve the results. The deviation between experiment and HFRS2PT results for the 2*s* level (mainly the GSC energy shift) increases with an increase of Z. However, the third-order terms describe the GSC energy shift much better. It is known that low value of the correlation energy calculated by the HFRS2PT for the ground-state neutral Be atom represents the well-known difficulties of this method in treating quasidegeneracy: quasidegeneracy of the $1s^2 2s^2$ and $1s^2 2p^2$ configurations in the neutral Be atom.[23] In contrast to the 1*s* pair correlation energy the 2*s* pair correlation energy calculated by the HFRS2PT is underestimated by a factor of 2 because of neglect of quasidegeneracy of the $1s^2 2s^2$ and $1s^2 2p^2$ configurations.[23] The calculations of the total correlation energy of four-electron isoelectronic series by the DHFRS2PT theory also shows that the correlation energy becomes much more underestimated by the DHFRS2PT with an increase of Z.[22] The HFRS5PT (fifth-order) result shows that the $2s^2$ pair correlation energy is much better improved ($\sim 50\%$). The HFRS5PT gives a good agreement with the full CI results since the $2s^2$ pair correlation energy represents a very significant contribution to the total correlation energy.[23] In the case of the 2*s* level, the nonhole hopping relaxation is dominating, and one can add the GSC energy shift calculated by the DHFRS2PT to the DHFΔSCF energy to see how the GSC energy is underestimated. The 2*s* energies obtained are almost equal to the DHFRS2PT energy. The discrepancy is only within 0.1 eV. The discrepancy between the DHFRS2PT and experiment is mainly due to the GSC energy which is underestimated. In the case of

TABLE III. Theoretical and experimental ionization energy of 1*s* core hole of the four-electron isoelectronic series (eV).

Z	g	g-Hartree	Expt.	Exact g
4	0.7234	-122.9	-123.6	0.7198
6	0.7225	-339.0		
8	0.7221	-664.4		
10	0.7219	-1099.1		

the 1*s* level the $1s^2$ and $1s2s$ pair correlation energy is well approximated by the HFRS2PT.[23] Then the 1*s* GSC energy must be well approximated by the HFRS2PT. The 1*s* energies obtained as a sum of the DHFΔSCF energy and the 2PTGSC energy are 124.3 eV for $Z=4$, 340.3 eV for $Z=6$, 655.4 eV for $Z=8$, and 1099.8 eV for $Z=10$. The results are better than the DHFRS2PT and lie between the HFRS2PT and HFRS3PT results. This shows that in the case of the 1*s* level the relaxation energy shift is underestimated by the HFRS2PT. The $1s^2$ and $1s2s$ pair correlation energies calculated by the HFRS2PT and HFRS5PT differs very little.[23] The HFRS3PT improves the relaxation energy shift and gives better agreement with the results.

To summarize, the HFRS2PT tends to underestimate the ground-state correlation energy of the 2*s* level of the four-electron isoelectronic series much more with an increase of Z. For the 1*s* level the HFRS2PT underestimates the relaxation energy shift very much.

In Tables III and IV, I summarized the results by the g-H2PT. The present results for the 1*s* and 2*s* ionization energy of the neutral Be atom differ from those published in previous works[11,13] because of more accurate treatment of the numerical evaluation of unoccupied orbitals for Be.

For the g-Hartree results the energy shifts due to the relativistic effects like the Breit interaction, vacuum polarization, etc., are evaluated as follows. As the total energies evaluated with a fixed g value for both initial and final states have no physical relevance, the ΔSCF approach is not useful for the present purpose. The total relativistic contributions for the initial state are evaluated for the g value determined in a semiempirical way so that the g-mean-field total energy of the initial state is equal to the experimental total energy. The numerical evaluation was performed by using the g-Hartree mean-field code modified from the DHF code.[24] The total relativistic contributions of the initial state calculated by both g-*H* and DHF methods are of the same magnitude. In the present work the ionization energy shift by these relativistic effects considered by the lowest-order approximation are assumed to be the same for both g-H and DHF results.

TABLE IV. Theoretical and experimental ionization energy of 2*s* core hole of the four-electron isoelectronic series (eV).

Z	g	g-Hartree	Expt.	Exact g
4	0.8214	-8.04	-9.323	0.7951
6	0.804	-46.9	-47.887	0.7939
8	0.7995	-113.0	-113.896	0.7937
10	0.7982	-206.4	-207.27	0.7938

TABLE V. Semiempirically determined exact g values of the 2*s* core-hole ionization energy of the four-electron isoelectronic series.

Z	Expt.	Exact g	$E(g=0.7951)$
4	-9.323	0.7951	-9.323
5	-25.137	0.7944	-25.08
6	-47.887	0.7939	-47.76
7	-77.742	0.7916	-77.301
8	-113.896	0.7937	-113.69
9	-157.161	0.7938	-156.92
10	-207.27	0.7938	-207.0

In contrast to the DHFRS2PT, the g-H2PT underestimates the 1*s* ionization energy for the neutral Be atom. However, the absolute deviation of theoretical result from experiment is much smaller than that of the DHFRS2PT and the agreement with experiment is good. Unfortunately the 1*s* core hole energies of the four-electron isoelectronic series are not available. One has to estimate the ionization energy in order to compare with the theoretical results. In Table V I listed semiempirically determined g values for the 2*s* level of the four-electron isoelectronic series. The g values are determined so that the g-mean-field eigenvalue becomes equal to the experimental ionization energy. I listed also the ionization energy of the 2*s* level evaluated for $g=0.7951$ which corresponds to the exact g value for the 2*s* level of the neutral Be atom. The deviations are within 0.8 eV and towards the less binding energy.

In Table VI I listed the 1*s*-level ionization energy evaluated for $g=0.7198$ which corresponds to the exact g value of the 1*s*-level ionization energy of the neutral Be atom. If the estimated experimental data are accurate, the HF2PT tends to give better agreement than the g-H2PT. The HFRS2PT tends to overestimate the binding energy for the 1*s* core-hole level; however, the deviation becomes smaller with an increase of Z. In the case of the 1*s* level of the four-electron isoelectronic series the HFRS2PT tends to underestimate the relaxation energy shift much less with an increase of Z.

The calculations of the total correlation energy of the four-electron isoelectronic series by the g-H second-order theory shows that the correlation energy tends to be overestimated much more with an increase of Z up to $Z=6$ and starts to approach to the exact result around $Z=10$.[22] For the 2*s* level the difference between the experiment and theory decreases with an increase of Z. This implies that the relaxation shift is overestimated for the 2*s* level by the g-*H* method; however, it begins to be less overestimated with an increase of Z. For the 1*s* level the difference between the experiment and theory increases with an increase of Z. This implies that with an increase of Z the relaxation shift for the 1*s* level of the four-electron isoelectronic series tends to be more overestimated by the g-H method.

However, one should note that when one uses the same g value for the different ionic states (different nuclear

TABLE VI. The 1*s* ionization energy of the four-electron isoelectronic series for $g=0.7198$.

Z	E ($g=0.7198$)	HFRS (second order)	HFRS (third order)	g-Hartree (second order)
4	-123.6	-124.9	-123.9	-122.9
5	-218.1	-219.1	-218.3	
6	-340.0	-340.6	-340.0	-339.0
7	-489.1	-489.5	-488.9	
8	-665.6	-665.6	-665.0	-664.4
10	-1100.6	-1100.1		-1099.1

charge), for the inner-shell ionization energy one should expect a much larger fluctuation. Note that the present *g*-Hartree ionization energies for the 1*s* core level of the isoelectronic series are about 0.4 eV higher than the DHF Δ SCF results which are in the case of the neutral atom 0.3 eV higher than the experiment. This tendency may remain even when the nuclear charge increases. Then the *g*-H method gives a good agreement with the experiment.

IV. CONCLUSIONS

The analysis of present DHFRS2PT and *g*-H2PT results implies the following.

(i) For the 1*s* level of the four-electron isoelectronic series the relaxation energy shift tends to be underestimated much less with an increase of Z by DHFRS2PT and tends to be overestimated much more with an increase of Z by *g*-H2PT.

(ii) For the 2*s* level of the four-electron isoelectronic series the ground-state correlation energy tends to be underestimated much more with an increase of Z by the DHFRS2PT and the relaxation energy shift tends to be overestimated much less with an increase of Z by the *g*-H2PT.

(iii) The present *g*-H2PT calculations were performed within the framework of the constant *g*-value method. However, the scope of *g*-Hartree theory is much wider: g is, in general, space dependent. The numerical calculations using the space-dependent *g*-H2PT are now in progress. The results will be presented in a forthcoming paper.

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