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g-Hartree *ab initio* calculation of ionization energies of Ca ($Z=20$)

Masahide Ohno
Physikalisches Institut, der Universität Bonn, Nussallee 12, 5300 Bonn 1, West Germany

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The main atomic ionization energies of Ca ($Z=20$) are calculated by the *g*-Hartree method. The agreement between theory and experiment is excellent. A detailed comparison of present method with other approximation schemes is made.

I. INTRODUCTION

During the last decade, the *ab initio* calculations of ionization energies (potentials) by many-body formalism have attracted much interest.[1-5] In contrast to conventional configuration-interaction (CI) and multiconfiguration self-consistent field (MCSCF) methods by which one obtains the ionization energy as a difference in total energies, the ionization energy can be obtained directly by many-body formalism. The results are often more accurate than those obtained by conventional methods. This is mainly because of a more balanced treatment of both initial and final states.

Recently the new systematic scheme for the *ab initio* calculation of the transition energy was proposed within the framework of the *g*-Hartree mean-field method.[6] The *g*-Hartree method is a mean-field method derived exactly from the fully relativistic QED action by using the functional integral method.[7] The *g*-Hartree mean field allows for optimization according to the physical quantity of interest: *g* can be chosen such that correlations (defined by deviation from the results predicted by the independent-particle picture) vanish. The determination of optimal mean field requires the solution of a nonlinear self-consistency equation and is fully *ab initio*; parameters are the fine-structure constant and the electron mass. This *g*-Hartree method was extended so that the electron energy levels in this mean field, i.e., the eigenvalues of the *g*-Hartree equation, are equal to the theoretically exact ionization energies: An exact version of the Koopmans theorem was derived.[6] The Koopmans theorem[8] originally derived for Hartree-Fock (HF) formalism has no physical relevance in the sense that the correlations are completely neglected in the HF theory. This mean field is determined by a perturbative calculation of *g*. The major advantage of *g*-Hartree transition energy calculations is that the method is fundamentally based on a renormalizable algorithm derived from the QED action in a rigorous manner. The computations proceed by a systematic hierarchy of approximations.

In a previous work[6], it is shown that the results obtained by the *g*-Hartree second-order calculations give excellent agreement with experiment for the atomic levels of He ($Z=2$), Li ($Z=3$), Be ($Z=4$), Ne ($Z=10$), Mg ($Z=12$), and Ar ($Z=18$). With an increase in atomic number, more dramatic many-electron effects are expected in the photionization spectra from localized core levels from atoms and solids. Pronounced final (ionic) -state correlation effects are found for the Ca ($Z=20$) *M*-shell ionization due to a drastic change of the $3d$ wave function which is drawn closer to the nucleus by the stronger central field experienced when an *M*-shell electron is ejected.[9] Many-body calculations using HF basis sets show that in particular the relative intensity of the $3s$ main ionic state is reduced significantly and shifted as much as ~ 4 eV from the relativistic Hartree-Fock ΔSCF binding energy (where ΔSCF represents the change in the self-consistent field) due to strong mixing of the $3s$ hole with the $3p^4 3d 4s^2$ configuration.[10-12] When the experimental atomic data for the binding energies are not available as in the case of the $3s$ level of Ca, it would be very important to be able to predict accurately the atomic ionization energy. In the present work the major atomic levels of Ca (only main ionic states) are calculated by the *g*-Hartree method using the *g*-Hartree computer code recently developed. The results obtained for the main ionic states are in excellent agreement with the available experimental and estimated atomic values. The results for the atomic level of He ($Z=2$), Be ($Z=4$), Ne ($Z=10$), Mg ($Z=12$), and Ar ($Z=18$) by the new *g*-Hartree code will be reported elsewhere.[13]

II. THEORY

We repeat briefly the derivation of the *g*-Hartree perturbative expansion for transition energies in atomic states (see Ref. 6 for a more detailed account). We note that we use the full relativistic QED action as the starting point; however, we present the derivation within the simplified model defined by the nonrelativistic action. The quantity to be evaluated is the partition function

$$Z(\beta,\mu)=\int \mathscr{D}\varphi e^{S[\varphi]} , \tag{2.1}$$

where μ denotes the chemical potential, β is the inverse temperature $(kT)^{-1}$, and S is the action. The ground-state energy is given by

$$E=-\lim_{\beta\to\infty} \beta^{-1}\ln Z . \tag{2.2}$$

We expand the partition function around a "time"-independent field which is *not* assumed to be a stationary point of the functional integral. We note the total energy as

$$E=E_{\varphi_0}[n_\alpha] \tag{2.3}$$

to indicate the dependence on the atomic configuration n_α and the field around which we choose to expand perturbatively. Note that the total energy does not depend on φ_0 around which it is expanded but the degree of approximation by a finite number of terms *does* indeed depend on φ_0.

For the transition $\{n_\alpha^{(i)}\}\rightarrow\{n_\alpha^{(f)}\}$, a transition energy can be written as

$$\Delta E = E_{\varphi_0^{(f)}}[n_\alpha^{(f)}]-E_{\varphi_0^{(i)}}[n_\alpha^{(i)}] \ . \tag{2.4}$$

Here the reference fields for the perturbative expansion $\varphi_0^{(i)}(\mathbf{x},\mathbf{x}')$ and $\varphi_0^{(f)}(\mathbf{x},\mathbf{x}')$ can, in general, be chosen differently. Our present choice is the following:

$$\varphi_0^{(i)}=\varphi_0^{(f)}=\varphi_{g\text{-}H}[n_\alpha^{(i)}] \ , \tag{2.5}$$

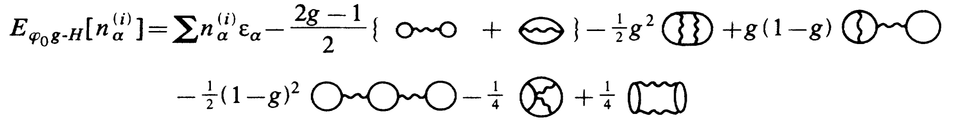
where the *g*-Hartree field is obtained from the *g*-Hartree equations for the initial configuration $\{n_\alpha^{(i)}\}$, i.e.,

$$\left[D_{\text{kin}}+V_{\text{ext}}(\mathbf{x})+\sum_\alpha n_\alpha^{(i)}\int d^3x' V(\mathbf{x},\mathbf{x}')[g\ |\psi_\alpha(\mathbf{x}')|^2-(1-g)\psi_\alpha(\mathbf{x})\psi_\alpha^*(\mathbf{x})^*]\right]\psi_\beta(\mathbf{x})=\varepsilon_\beta\psi_\beta(\mathbf{x}) \ . \tag{2.6a}$$

$$V(\mathbf{x},\mathbf{x}')=\frac{e^2}{|\mathbf{x}-\mathbf{x}'|} \ . \tag{2.6b}$$

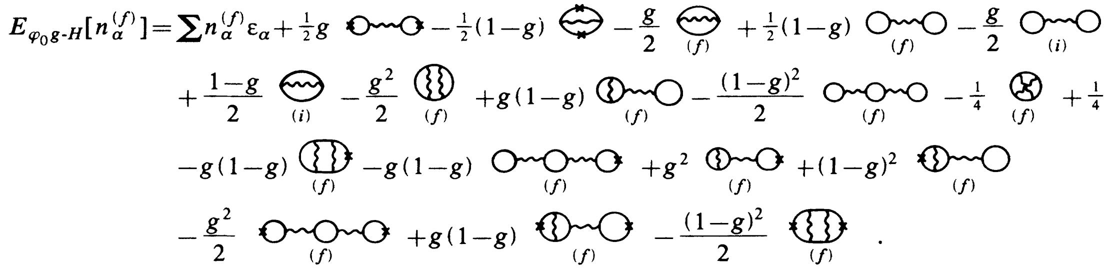
Here D_{kin} is the relativistic or nonrelativistic kinetic energy of free electrons and $V_{\text{ext}}(\mathbf{x})$ is the nuclear Coulomb potential.

The graphical representation of the total energy for the initial and final configurations $\{n_\alpha^{(i)}\}$ and $\{n_\alpha^{(f)}\}$ are



(2.7)

and

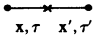


(2.8)

Here the graphical notations are

$V(\mathbf{x},\mathbf{x}')\delta(\tau-\tau')$

$$g(\mathbf{x},\mathbf{x}';t)\,|_{t=i(\tau-\tau')}$$
$$=-i\sum_\alpha \psi_\alpha(\mathbf{x})\psi_\alpha^*(\mathbf{x}')e^{-i(\varepsilon_\alpha-\mu)t}$$
$$\times[\theta(t)-n_\alpha]\,|_{t=i(\tau-\tau')} \tag{2.9}$$



$$\kappa(\mathbf{x},\mathbf{x}';\tau-\tau'):=$$
$$\sum_\alpha (n_\alpha^{(f)}-n_\alpha^{(i)})\psi_\alpha(\mathbf{x})\psi_\alpha^*(\mathbf{x}')\delta(\tau-\tau') \ ,$$

where $a:=b$ represents a defined by b. Here the crossed electron propagator in (2.9) in the *g*-Hartree field represents the instantaneous propagation of levels which change in the transition $\{n_\alpha^{(i)}\}\rightarrow\{n_\alpha^{(f)}\}$. In general the transition energy ΔE can be written as

$$\Delta E=\sum_\alpha (n_\alpha^{(f)}-n_\alpha^{(i)})\varepsilon_\alpha+\sum_{i=1}^{\infty}E_i^{\text{corr}}(g;n_\alpha^{(i)}\rightarrow n_\alpha^{(f)}) \ , \tag{2.10}$$

where the index i counts the number of instantaneous Coulomb interactions. We determine g_1 such that contributions of correlations to the transition energy vanish,

$$\sum_{i=1}^{K}E_i^{\text{corr}}(g;n_\alpha^{(i)}\rightarrow n_\alpha^{(f)})\,|_{g=g_1}=0 \ . \tag{2.11}$$

We then have

$$\Delta E=\sum_\alpha (n_\alpha^{(f)}-n_\alpha^{(i)})\varepsilon_\alpha \tag{2.12}$$

to be prescribed order K of electron-electron interactions; an exact version of the Koopmans theorem.

For the single-hole ionization energy we take

$$\begin{aligned} n_\alpha^{(i)}&=n_\alpha^{(f)} \text{ for } \alpha\neq\alpha_0 \ , \\ n_\alpha^{(i)}&=n_\alpha^{(f)}+1 \text{ for } \alpha=\alpha_0 \ . \end{aligned} \tag{2.13}$$

Then we obtain

$$\Delta E = \varepsilon_{\alpha_0} . \tag{2.14}$$

For the Auger transition ($i^{-1} \to j^{-1}k^{-1}\varepsilon l$) energy, we obtain

$$\Delta E = \varepsilon_i - \varepsilon_j - \varepsilon_k . \tag{2.15}$$

Here $\varepsilon_x (x = i,j,k)$ are the eigenvalues of the singly ionized (i^{-1}) hole state. We determine numerically g_1 by solving the g-Hartree equation (2.6) and Eq. (2.10) alternatively in an iterative routine. Note that the energy level ε_α are the eigenvalues of the g-Hartree equation obtained for $g = g_1$.

In the present work we performed the second-order g-Hartree calculations as in a previous work[6] where we obtained excellent agreement with experiment. The Dirac-Hartree-Fock computer code by Johnson[14] was adapted to the g-Hartree approach. This new g-Hartree code was used to generate basis sets necessary for the calculations of diagrams. Numerical accuracy and reliability of virtual (discrete and continuum) orbitals is improved. Furthermore, the new version of computer code for numerical evaluation of g-Hartree diagrams was developed for the present work.[15] Magnetic contributions to the ionization energy are computed by using self-consistent g_1 orbitals. They turn out to be negligible for the atomic levels considered. Note that we neglect antiparticle states in the spectral sums of Eq. (2.10). This is equivalent to neglecting dynamical relativistic corrections which are of great interest in the study of the quantum structure of the physical vacuum.[16]

III. RESULTS AND DISCUSSION

The present results for Ca by the g-Hartree method are listed in Table I with the theoretical results by other methods. The agreement of the present results by the g-Hartree method with the experiment is excellent. First, we should comment on the experimental data quoted here. The experimental data for $3p$ and $4s$ levels are taken from the atomic data.[9,17–19] However, as the atomic data for the $2s$ and $3s$ levels are not available, they are approximately obtained from the solid-state data[20] by using the theoretical atom-solid binding energy calculated by Johansson and Mårtensson[21] (within the accuracy of ∼0.5 eV).

Here we comment briefly on the methods used for other theoretical results listed in Table I. Dirac-Hartree-Fock (DHF) eigenvalues (so-called Koopmans energy) are obtained by solving a DHF equation. DHF ΔSCF energies are obtained as the differences of the total energy of the neutral ground state and ionic state calculated separately. The DHF ΔSCF results improve the results; however, the correlations are completely neglected. The deviation from the Koopmans energy (corrections to the Koopmans theorem) is interpreted in terms of relaxation (correlations) and calculated by perturbation theory. The methods to calculate the corrections to the Koopmans theorem by using the Hartree-Fock-like basis sets can be in general categorized into two major approaches. One is the configuration-interaction (CI) method by which one expands the fixed one-particle basis set in terms of a large number of configuration. The other one is the Green's-function method by which one obtains the ionization energy and intensities as the pole and its residue of the one-particle Green's function. (See Ref. 6 for the extensive compilation of methods employed for the ionization energy calculations of small atoms.) Walter and Schirmer[10] used the one-particle Green's-function method within the framework of the extended two-particle—one-hole (or two-hole—one-particle) Tamm-Dancoff approximation [$2p$-$1h$ ($2h$-$1p$)—TDA] method. By employing the self-energy which is exact up to the third order of perturbation theory, this method overcomes the major shortcoming of the $2p$-$1h$—TDA method: neglect of some third-order contributions of the energy-dependent self-energy which are related to the ground-state correlation. In other words, the ground-state correlation is only partly accounted for. Their extended $2p$-$1h$—TDA method also gives

TABLE I. Theoretical and experimental ionization energies of Ca ($Z=20$) (units of eV).

Level	g-H (g_0)	DHF (Koopmans)	DHF ΔSCF	$2p$-$1h$—TDA[a]	$2p$-$1h$—CI[b]	RPAE[c]	Expt.
$2s$	448.8 ($g = 0.8882$)	461.7	450.0				448.2
$3s$	53.88 ($g = 0.9324$)	61.55	58.78	53.89	52.16 (51.03)	54.4	53.89
$3p_{1/2}$	34.62 ($g = 0.9341$)	36.71	34.00	34.43	32.88 (32.77)		34.67[d] 34.66[e]
$3p_{3/2}$	34.26 ($g = 0.9341$)	36.29	33.62				34.33[d] 34.31[e]
$4s$	6.38 ($g = 0.9493$)	5.34	5.14	6.13	5.07		6.113[f] 6.11[g]

[a] Reference 10.
[b] Reference 11.
[c] Reference 12.
[d] Reference 18.
[e] Reference 9.
[f] Reference 19.
[g] Reference 17.

excellent agreement with the experiment.

Because of relatively lower accuracy of treatment of satellite states by the $2p$-$1h$—TDA Green's-function method, De Alti *et al.*[11] have performed $2h$-$1p$ space CI calculations. Their results are in excellent agreement with the results by the $2h$-$1p$—TDA method for the energies and intensities of shake-up states due to a more uniform treatment of all ionic $2h$-$1p$ states. However, as shown in Table I, their results tend to underestimate the main ionization energies. In these two methods, because of the difficulties stemming from the incomplete set of virtual HF orbitals, the double-ionization continuum states are not properly treated. However, the effects of the coupling to the continuum results not only in a broadening of the energy level but also in an energy shift. The one-particle Green's-function method which explicitly includes the interaction with the continuum has been used extensively by Wendin and Ohno.[22–25] The self-energy is calculated within the framework of RPAE (random-phase approximation with exchange). This method has been extensively applied to calculate the x-ray photoemission, x-ray emission, and Auger-electron spectra of several localized core levels of a wide range of atomic elements. The results calculated by the author using this method are also listed in Table I. The detailed account of the method and results will be published elsewhere.[12]

In the methods mentioned above one includes the higher-order corrections by summing up the selected diagrams to the infinite order (RPAE), or exactly to the third order ($2p$-$1h$ TDA) for the self-energy, and then by an infinite partial summation of the self-energy via the Dyson equation. However, the present g-Hartree calculation is a truly second-order determination of the optimal mean field. Furthermore, none of the other methods is fundamentally based on a renormalizable algorithm derived from the QED action in a rigorous manner. In general, with the perturbation approaches using Hartree-Fock-like basis sets, there is no control over (or estimate of) the next order of approximation. It should be noted that a third-order calculation does not necessarily improve the second-order result [e.g., for the Ne ($Z=10$) case see Refs. 26 and 27]. However, the g-Hartree method allows for a certain control of higher-order contributions (see Ref. 6 for a detailed account). We refer to a previous work[6] for further detailed discussions on the g-Hartree method in comparison with other approaches.

IV. CONCLUSIONS

g-Hartree *ab initio* calculation of main ionization energies of Ca ($Z=20$) shows excellent agreement with experiment. The present g-Hartree *ab initio* calculation is truly second order in contrast to the other theoretical results obtained by the methods which include the higher-order terms.

In the present work we limited ourselves to the calculation of the ionization energy of main ionic state; however, the present formalism allows us to calculate the shake-up satellites and Auger excitation energy. We leave the g-Hartree *ab initio* calculation of shake-up satellite and Auger excitation energy to the future.

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[1] L. S. Cederbaum and W. Domcke, in *Advances in Chemical Physics,* edited by I. Prigogine and S. A. Rice (Wiley, New York, 1977), Vol. 36, p. 205.

[2] Y. Öhrn and G. Born, in *Advances in Quantum Chemistry,* edited by P.-O. Löwdin (Academic, New York, 1981), Vol. 13, p. 1.

[3] M. F. Herman, K. F. Freed, and D. L. Yeager, in *Advances in Chemical Physics,* edited by I. Prigogine and S. A. Rice (Wiley, New York, 1981), Vol. 48, p. 1.

[4] V. Kvasnicka and I. Hubač, J. Chem. Phys. **60**, 4483 (1974).

[5] G. Wendin, *Structure and Bonding* (Springer, Berlin, 1981), Vol. 45, p. 1, and references therein.

[6] K. Dietz, M. Ohno, and G. Weymans, J. Phys. B **19**, 2995 (1986).

[7] K. Dietz, O. Lechtenfeld, and G. Weymans, J. Phys. B **15**, 4301 (1982).

[8] T. Koopmans, Physica **1**, 104 (1934).

[9] M. W. D. Mansfield and G. H. Newsom, Proc. R. Soc. London, Ser. A **357**, 77 (1977).

[10] O. Walter and J. Schirmer, J. Phys. B **14**, 3805 (1981).

[11] G. De Alti, P. Devleva, and A. Lisini, Chem. Phys. **93**, 225 (1985).

[12] M. Ohno (unpublished).

[13] M. Ohno, Z. Phys. D (to be published).

[14] W. R. Johnson (unpublished).

[15] M. Ohno (unpublished).

[16] K. Dietz and G. Weymans, J. Phys. B **17**, 4801 (1984).

[17] S. Süzer, S. T. Lee, and D. A. Shirley, Phys. Rev. A **13**, 1842 (1976).

[18] W. Schmitz, B. Breuckmann, and W. Mehlhorn, J. Phys. B **9**, L493 (1976).

[19] C. E. Moore, *Atomic Energy Levels,* Natl. Bur. Stand. (U.S.) Circ. No. 467 (U.S. GPO, Washington, D.C., 1949), Vol. 1.

[20] J. C. Fuggle and N. Mårtensson, J. Electron Spectrosc. Relat. Phenom. **21**, 275 (1980).

[21] B. Johansson and N. Mårtensson, Phys. Rev. B **21**, 4472 (1980).

[22] G. Wendin and M. Ohno, Phys. Scr. **14**, 148 (1976).

[23] M. Ohno and G. Wendin, J. Phys. B **11**, 1557 (1978); **12**, 1305 (1979).

[24] M. Ohno, Phys. Scr. **21**, 589 (1980); J. Phys. C **13**, 447 (1980); J. Phys. B **17**, 195 (1984); Phys. Rev. B **29**, 3127 (1984).

[25] M. Ohno and G. Wendin, Phys. Rev. A **31**, 2318 (1985).

[26] L. S. Cederbaum and W. von Niessen, Chem. Phys. Lett. **24**, 263 (1974).

[27] H. Yamakawa, T. Aoyama, and H. Ichikawa, Chem. Phys. Lett. **47**, 269 (1977).