PHYSICAL REVIEW A **85**, 052512 (2012)

Particle-hole configuration-interaction polarizabilities and Verdet constants of noble-gas atoms

I. M. Savukov
Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

(Received 12 March 2012; published 24 May 2012)

Polarizabilities and Verdet constants are calculated using a relativistic particle-hole configuration-interaction (CI) method. Particle-hole CI is saturated by including quasicontinuum states built by enclosing an atom in a cavity. Agreement with experiment is achieved, and the method is more accurate than, for example, the Hartree-Fock method. The accuracy of the particle-hole CI method is limited by the omission of configurations with double excitations. Perturbation theory can be applied to account for these excitations, and we expect in the future to further improve the accuracy. The method can be also applied to the calculations of polarizabilities of excited states and can be generalized to other open-shell atoms.

DOI: 10.1103/PhysRevA.85.052512 PACS number(s): 31.15.am, 31.30.jc, 32.30.Dx

I. INTRODUCTION

Atomic polarizability has been accurately evaluated in noble gases and has been used to test theory. For example, the polarizability of the helium ground state has been studied with very high precision, with experimental precision reaching 5 ppm and theoretical results quoted with six to nine digits. The agreement between theory and experiment has been found at the level of 0.05% (see, for example, Ref. [1]). The experimental precision in other noble-gas atoms is somewhat lower, with four to five digits quoted, and the theoretical precision is even lower [2]. The loss of theoretical precision is due to extra complexity of these multielectron atoms in which correlation corrections are difficult to take into account. However, from this point of view it is quite remarkable that theories show worse agreement in neon than in heavier noble-gas atoms. This is one motivation for conducting theoretical analysis in this paper with some focus on the neon atom. In general, agreement between experiment and some theories is on the order of 10% [2]. The coupled-cluster theory with energy-adjusted pseudopotentials that includes single, double, and triple excitations gives good agreement with experiment for all noble-gas atoms. Static and dynamic polarizabilities are related to refractive indices, with static in the limit of long wavelengths and dynamic at arbitrary wavelengths. These quantities can be measured directly in experiment and accurately in gases and calculated with similar methods to polarizabilities. In addition to testing theories, polarizability is used for constructing model potentials and in many other applications [3]. The Verdet constant is yet another quantity related to dynamic polarizability that can be directly measured in experiment.

In this paper, we use the framework of particle-hole configuration-interaction (CI) and relativistic many-body perturbation theory (RMBPT) to calculate polarizabilities and the derived properties, such as refractive indices and Verdet constants. RMBPT is a powerful method for treating multielectron atoms and ions. To apply it to atoms and ions with two or more valence electrons the so-called mixed CI + RMBPT has been developed, and good precision for energies and transitions has been demonstrated in a number of atoms. The CI + RMBPT approach is difficult to apply to particle-hole states of closed-shell atoms due to poor convergence of RMBPT. Previously, we developed a reliable particle-hole CI + RMBPT approach for noble-gas atoms and demonstrated agreement with experiment for energies, oscillator strengths [4–7], and g factors [8]. This theory can be applied to calculations of polarizabilities and Verdet constants. However, particle-hole CI + second-order RMBPT was applied to the lowest states, but the calculations of transitions to continuum levels have the difficulty of small denominators that can appear randomly in second-order perturbation terms. To avoid this problem, we removed the RMBPT part of the theory, that is, reduced it to the particle-hole CI.

We calculate polarizability and derive properties by summing the particle-hole CI oscillator strength (OS) over the complete spectrum that includes quasicontinuum contributions. The CI states are formed as linear combinations of discrete Dirac-Hartree-Fock (DHF) V^n B-spline basic functions. For comparison, we also perform calculations by summing relativistic DHF OSs in the V^n basis. We find that although DHF polarizabilities agree with experiment, this agreement is fortuitous because of cancelations of correlation corrections.

We demonstrate that the particle-hole CI formalism can be used to obtain reliable values of polarizabilities and Verdet constants for noble-gas atoms. Theory can be further improved by including second-order RMBPT corrections or by expanding single particle-hole CI to two-particle–two-hole CI, which is beyond the scope of this paper due to the above-mentioned difficulties with denominators or the extra complexity of the two-particle–two-hole CI approach. One method to avoid denominator difficulties could be the Brillouin-Wigner variant of perturbation theory, in which the ground-state energy is used so that the denominators will be always negative. It is also known that this theory works near degeneracy. Thus this could be the most promising approach. Unfortunately, the current codes have to be significantly modified to accommodate the required changes and tested with energy and transition calculations. Also, other CI methods, such as two-particle, three-particle, etc., CI can be applied to polarizability calculations of a large number of atoms using DHF B-spline bases and the approach of summing OSs over the complete spectrum demonstrated here. It is also possible to use the hybrid approach in which low-energy OSs are calculated with CI + the second-order RMBPT and high-energy OSs are taken from experiment or other theories more suitable for continuum states.

This work is also motivated by the need to develop a reliable *ab initio* theory for calculations of the so-called nuclear spin optical rotation (NSOR) effect [9]. This effect is quite similar to the Faraday effect, that is, polarization rotation by a magnetic field, but, instead of an external field, the field of the atomic nucleus is the cause of light polarization rotation. For NSOR calculations, it is important to include or evaluate contributions from the full spectrum. The distribution of spectral contributions for NSOR can be quite different than that for polarizability. So to cross-check the theory, it is important to have agreement not only for a single quantity such as polarizability but also for the Verdet constant and OS sum rules. Eventually, NSOR theory based on CI and RMBPT can be extended to molecules and condensed-matter systems. Relativistic effects are expected to be significant (they are substantially enhanced because of the importance of the behavior of wave function near the nucleus), so fully relativistic treatment, CI + RMBPT, is preferable.

II. THEORETICAL CALCULATIONS AND ANALYSIS

A. RMBPT framework

The starting point of our calculations is the solution of the DHF equation for a closed-shell atom to obtain the V^n potential for core electrons. Then the DHF equation is solved for this frozen-core potential in a B-spline basis. To make the basis discrete and compact the atom is placed in a spherical cavity, whose radius is chosen to minimize the effect of the cavity on the lowest states. Forty splines are chosen for each relativistic spin-angular index, and the maximum angular momentum is restricted to 5. Angular reduction, that is, summation over the magnetic sublevels, is performed for the perturbation terms. We use the same V^n basis for DHF and particle-hole CI calculations. DHF values are calculated for comparison.

B. DHF V^n approximation

Static scalar DHF polarizability expressed in atomic units in the case of closed-shell atoms is

$$\alpha_c = \frac{2}{3}\sum_{am}\frac{|\langle a\|r\|m\rangle|^2}{E_m - E_a}. \tag{1}$$

Here angular reduction is already carried out; a denotes hole states, m denotes excited states, and E is the energy. We calculate reduced dipole matrix elements $\langle a\|r\|m\rangle$ using radial B-spline DHF wave functions, which were described above.

The dynamic polarizability at low frequency ω, more precisely, away from resonances, is calculated by modifying the previous expression to include frequency dependence (see, for example, Ref. [10]):

$$\alpha_d(\omega) = \frac{2}{3}\sum_{am}\frac{(E_m - E_a)|\langle a\|r\|m\rangle|^2}{(E_m - E_a)^2 - \omega^2}. \tag{2}$$

The refractive index n in a very general case is related to the dynamic polarizability:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi N\alpha_d(\omega)a_0^3}{3}, \tag{3}$$

where N is the number of atoms per cm^3, $\alpha_d(\omega)$ is the polarizability in atomic units, and a_0 is the Bohr radius in cm. Because the refractive index is proportional to N, it is often given for a gas at STP with $N = 2.68709 \times 10^{19}$ cm^{-3}. In dilute gas, n is also very close to unity, so

$$n^2 - 1 = 5.004 \times 10^{-3}\alpha_d. \tag{4}$$

The Verdet constant can be calculated from the derivative of the refractive index [11] (in units of μmin Oe^{-1} cm^{-1} at STP):

$$V = 1.024 \times 10^6\omega\frac{\partial n}{\partial\omega}. \tag{5}$$

Our calculated DHF polarizabilities and Verdet constants are given in Table I.

C. Relativistic particle-hole CI method

The CI method is expected to be more accurate than DHF because it includes first-order corrections due to particle interactions. It can also be applied to arbitrary open-shell atoms. In this paper we focus on the particle-hole system, for which we have developed a CI + RMBPT theory. Second-order corrections introduce questions about the denominators, and we postpone the solution of the problem for future research in this direction. In this paper, we consider only the first-order CI + RMBPT, which also can be called the particle-hole CI method. In the CI method energy denominators do not appear. To find energies and wave functions of particle-hole states of closed-shell atoms, we introduce the orthogonal set of orbitals for particle-hole states defined as (see, for example, Ref. [17] for detail on notations)

$$\Phi_{JM}(av) = \sqrt{2J+1}\sum_{m_a,m_v}(-1)^{j_v-m_v} \times \begin{pmatrix} j_v & J & j_a \\ -m_v & M & m_a \end{pmatrix} a^\dagger_{vm_v}a_{am_a}|0\rangle. \tag{6}$$

The first-order Hamiltonian between these states is

$$H^{(1)} = \delta_{vv'}\delta_{aa'}(\varepsilon_v - \varepsilon_a) + \frac{1}{2J+1}(-1)^{j_v+j_a+J+1}Z_J(av'va'). \tag{7}$$

We chose the configurations with the hole states a running over all core states (for example, neon has core states $1s, 2s_{1/2}, 2p_{1/2}, 2p_{3/2}$) and with excited states v running over possible excited states up to the limit of 30 for the radial spline number. We created 40 spline orbitals for each spin-angular momentum number, and the result is saturated by including only 30 spline orbitals. After diagonalization of the Hamiltonian $H^{(1)}$, the states are formed as linear combinations of particle-hole orbitals:

$$\Psi_i = \sum_{av} C_i(av)\Phi_{JM}(av). \tag{8}$$

Using configuration expansion of reduced matrix elements of r,

$$r_i = \sum_{av} C_i(av)\langle a\|r\|v\rangle(-1)^{j_a-j_v}, \tag{9}$$

we can find the sums of oscillator strengths, static and dynamic polarizability, refractive indices, and Verdet constants by

TABLE I. Our calculations [particle-hole (ph) CI and V^n DHF] of polarizabilities and Verdet constants (μmin Oe^{-1} cm^{-1} at 750 nm) and comparison with theories and with empirical values of [12].

	ph CI	V^n DHF	Theory	Ref. [12]	Expt.
Helium					
α	1.398	1.272	1.383193[a]	1.384	
V	0.277	0.098	0.261[b], 0.259[c]	0.281	
Neon					
α	2.58	1.98	2.693[d]	2.633	2.669[e], 2.678[f]
V	0.422	0.157	0.475[b], 0.393[c]	0.542	
Argon					
α	12.8	10.2	11.073[d]	11.08	11.08[e], 11.221[f]
V	5.41	2.2	4.74[c]	5.27	
Krypton					
α	19.7	15.8	17.064[d]	16.7	16.79[e], 17.075[f]
V	11.36	4.56	9.94[c]	10.589	
Xenon					
α	32.8	26.8	27.658[d]	27.29	27.16[e], 27.815[f]
V	27.6	10.9	24.1[c]	23.65	

[a] Reference [1].

[b] Fully coupled HF of [13].

[c] Time-dependent DHF of [14], quadratically interpolated to 750 nm.

[d] Coupled-cluster single-double calculations with energy adjusted pseudopotentials and tripple excitations added perturbatively of [2].

[e] Reference [15].

[f] Reference [16].

summing r_i over all possible $J = 1$ odd excited particle-hole states i:

$$\mu_0 = \sum_i f_i = \sum_i \frac{2}{3}\omega_i r_i^2, \tag{10}$$

$$\mu_{-1} = \sum_i f_i/\omega_i = \sum_i \frac{2}{3} r_i^2, \tag{11}$$

$$\mu_{-2} = \sum_i f_i/\omega_i^2 = \sum_i \frac{2}{3}\frac{r_i^2}{\omega_i} = \alpha, \tag{12}$$

$$n^2 - 1 = 5.004 \times 10^{-3}\frac{2}{3}\sum_i \frac{\omega_i r_i^2}{\omega_i^2 - \omega^2}. \tag{13}$$

The Verdet constant can be calculated from Eq. (5).

The sum of OSs can be used as a test of completeness since it is known that this sum has to be equal to the number of electrons in the atom (the Thomas-Reiche-Kuhn rule). For neon we obtained this sum equal to 11.3 independently of various parameters that might affect the completeness of the basis: the maximum radial number varied from 30 to 35, and the cavity size varied from $R = 60$ a.u. to $R = 40$ a.u. An accurate sum must equal 10, the number of electrons in the neon atom, so we have 11% deviation. Two papers reported better values, 9.86 [18] and 10.32 [19]. Because, for the total sum of oscillator strengths, high-energy photoionization OSs are important, we are not surprised that we found some deviation. On the other hand, the sums of oscillator strengths that are divided by energies and hence are less sensitive to high-energy contributions are in better agreement: our result for μ_{-1} is 2.03 and is different by only 3.5% and 5.4% from the values of 1.96 and 1.922 reported in Refs. [18,19], respectively; for μ_{-2} our value 0.64 is 4.5% different from the value of 0.67 reported in Refs. [18,19].

Our particle-hole CI values of static dipole polarizability and Verdet constants at 750 nm are listed in Table I. Verdet constants in the spectral range 375–1000 nm are plotted in Fig. 1 and are given for several wavelengths in Table II.

III. DISCUSSION

A. Comparison of DHF and particle-hole CI

Accurate polarizability assumes the summation over accurate OSs with correlations included, so a particle-hole CI that includes the interaction between a particle and a hole in the

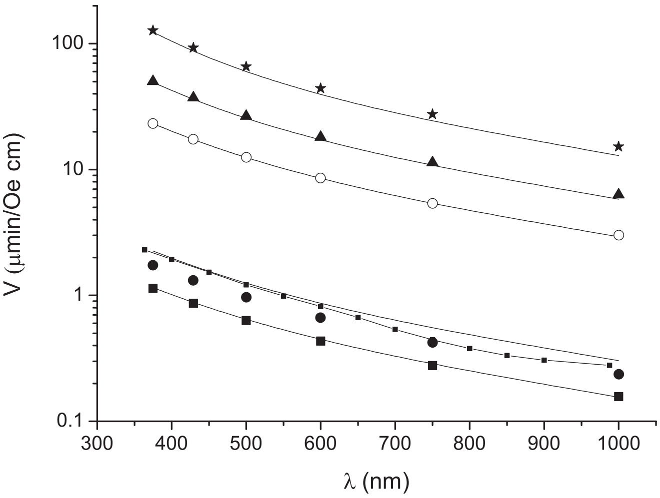

FIG. 1. Comparison of our particle-hole CI Verdet constants (large squares, He; solid circles, Ne; open circles, Ar; triangles, Kr; stars, Xe) with values from [12] (solid curves) and the experimental measurements of [20] (solid curve with small squares).

TABLE II. Particle-hole CI Verdet constants (in μmin Oe^{-1} cm^{-1}).

λ (nm)	He	Ne	Ar	Kr	Xe
375	1.14	1.75	23.2	50.1	127
429	0.865	1.32	17.4	37.2	92.9
500	0.631	0.964	12.5	26.6	65.6
600	0.435	0.664	8.56	18.1	44.1
750	0.277	0.423	5.41	11.4	27.5
1000	0.155	0.237	3.01	6.30	15.2

excited states of closed-shell atoms is a better approximation than V^n DHF. The limited accuracy of DHF approximation is particularly clear in the case of helium. According to our calculations, V^n DHF polarizability is 1.272 and deviates by 8% from the accurate value of 1.384, while the particle-hole CI value of 1.398 deviates by only 1% (Table I). Poor agreement for helium is somewhat surprising because for other noble-gas atoms relatively good agreement of DHF V^n values with experiment can be observed. We attribute this to the cancellation of correlation corrections. However, DHF V^n Verdet constants, which are the derivative of the dynamic polarizability, are completely off for all noble-gas atoms, and the discrepancy increases from He to Xe, as expected from the increase of correlation corrections. The particle-hole CI method gives consistent agreement with experiment for Verdet constants for all noble-gas atoms in a large spectral range (Fig. 1).

B. Evaluation of error in calculations due to second-order effects

As we mentioned earlier, to avoid denominator problems in the continuum range, the second-order RMBPT corrections are excluded. While it is quite difficult to estimate the errors arising from multiple terms that are neglected, crudely, error can be estimated from the magnitude of large terms. One such large term gives a correction to the hole energy due to the second-order effect arising from the interaction of the hole with core electrons. In neon, we found that hole energy changed from 0.84 to 0.71 a.u., the sum of oscillator strength from 11.3 to 10.7, polarizability from 2.58 to 2.94 (12%), and the Verdet constant at 770 nm from 0.423 to 0.738 (70%). In argon, the hole energy changed from 0.588 to 0.519, polarizability from 12.8 to 14.3 (11%), the Verdet constant from 5.41 to 7.98 (50%), and the sum of the OS from 21.9 to 20.9. In Kr, the hole energy changed from 0.514 to 0.453, polarizability from 19.7 to 22.0 (11%), and the Verdet constant at 770 nm from 11.36 to 17.1 (50%). So it appears that polarizability is affected by the hole-energy change at the level of 10% and the Verdet constant at 770 nm at the level of 50%. A larger change occurs for the Verdet constant because it is more sensitive to the energy. Shifting only hole energy is not the most appropriate way to include second-order effects because the hole wave functions also change, and this effect can compensate for that of the energy change. Another way to estimate the error is to look at the difference between DHF calculations and particle-hole CI. The change in the Verdet constant was quite large, so indeed the Verdet constant is highly sensitive to correlation corrections. Particle-hole interaction is very important because it is on the order of unity and has to be treated at all orders, as we did in this paper. Second-order effects should be smaller, but they should be done carefully because there is strong cancellation between large terms. In our previous work we found that if second-order effects are added in the correct way, agreement for a large number of OSs and energies is achieved [4–7]. The evaluation of error discussed in this section is quite approximate, and a better evaluation of the theory is obtained by comparison with experiment for multiple atoms and wavelengths.

C. Comparison of particle-hole CI Verdet constants with experiment

In order to evaluate the accuracy of the particle-hole CI method, we compared polarizabilities and Verdet constants with reliable semiempirical interpolation equations given by Dalgarno and Kingston [12] which agree closely with experiment, except for the case of neon. For this reason, in Fig. 1 we added purely experimental data for neon. We also observed accurate agreement of our results for noble-gas atoms except for neon, which is also quite surprising. Purely experimental neon data agree better at 750 and 1000 nm with our results than values obtained from the interpolation of [12]. This raises some questions about experimental values of neon at other wavelengths where agreement was not as close as in all other cases considered.

D. Other theoretical calculations

Polarizabilities have been calculated with many methods. Very close agreement with experiment has been achieved in coupled-cluster single-double calculations with optimized basis sets and triple excitations added perturbatively with energy-adjusted pseudopotentials [2] (Table I). Our purely *ab initio* calculations are less accurate for polarizabilities, but this is expected considering the approximation of the first-order RMBPT. We expect that inclusion of second-order RMBPT corrections or some pseudopotentials to account for the omitted correlation corrections will improve agreement. One interesting point about our current calculations is that the basis is more or less complete at the level of particle-hole orbitals and our approach allows systematic treatment of correlations. The CI method with a complete discrete basis of an atom in a cavity can be applied to other atoms where CI configurations might be more complicated and extensive.

For Verdet constants, good agreement is obtained with four-component Hartree-Fock calculations for Ar, Kr, and Xe, but surprisingly very poor agreement is obtained for Ne and He [14]. This raises questions about this method. Good agreement is also obtained with the random-phase-approximation exchange (RPAE) method for Xe, but the results for the Verdet constants are not shown for other noble-gas atoms [21]. Our method predicts Verdet constants for all noble-gas atoms consistently, although in neon an anomaly exists. Although, in the case of helium, high precision is achieved with available accurate methods, here we considered helium to understand overall trends of our method and to show that DHF is inaccurate.

IV. CONCLUSION

We applied particle-hole CI theory built in the RMBPT framework to calculations of polarizabilities and Verdet constants and found a consistent agreement for all noble-gas atoms. The CI approach with a B-spline finite basis can be applied to other atoms. Currently, we excluded second-order RMBPT corrections because they contain denominators that can be randomly small, so correlations beyond the particle-hole interaction are excluded. This can be amended in the future after the CI + RMBPT approach is investigated for continuum state transitions, and it seems that the Brillouin-Wigner variant of perturbation theory can help to avoid the zero-denominator problem.

ACKNOWLEDGMENT

This work is supported by LDRD 20110487ER of Los Alamos National Laboratory.

[1] M. Masili and A. F. Starace, Phys. Rev. A **68**, 012508 (2003).

[2] A. Nicklass, M. Dolg, H. Stoll, and H. Preuss, J. Chem. Phys. **102**, 8942 (1995).

[3] K. D. Bonin and M. A. Kadar-Kallen, Int. J. Mod. Phys. B **8**, 3313 (1994).

[4] I. M. Savukov, W. R. Johnson, and H. G. Berry, Phys. Rev. A **66**, 052501 (2002).

[5] I. M. Savukov, Phys. Rev. A **67**, 022502 (2003).

[6] I. M. Savukov, J. Phys. B **36**, 2001 (2003).

[7] I. M. Savukov, J. Phys. B **36**, 4789 (2003).

[8] I. M. Savukov, J. Phys. B **45**, 045002 (2012).

[9] I. M. Savukov, S.-K. Lee, and M. V. Romalis, Nature (London) **442**, 1021 (2006).

[10] L. Barron, *Molecular Light Scattering and Optical Activity* (Cambridge University Press, Cambridge, 2004).

[11] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Clarendon, Oxford, 1932).

[12] A. Dalgarno and A. E. Kingston, Proc. R. Soc. London, Ser. A **259**, 424 (1960).

[13] V. G. Kaveeshwar, K. T. Chung, and R. P. Hurst, Phys. Rev. **172**, 35 (1968).

[14] U. Ekström, P. Norman, and A. Rizzo, J. Chem. Phys. **122**, 074321 (2005).

[15] A. Kumar and W. J. Meath, Can. J. Chem. **63**, 1616 (1985).

[16] U. Hohm and K. Kerl, Mol. Phys. **69**, 803 (1990).

[17] U. I. Safronova, C. Namba, I. Murakami, W. R. Johnson, and M. S. Safronova, Research Report NIFS-DATA-61, 2001, National Institute for Fusion Science (NIFS) of Japan (unpublished).

[18] K. G. Sewell, Phys. Rev. **138**, A418 (1965).

[19] K. R. Piech and J. S. Levinger, Phys. Rev. **135**, A332 (1964).

[20] L. R. Ingersoll and D. H. Liebenberg, J. Opt. Soc. Am. **44**, 566 (1954).

[21] A. R. Tančić and M. Davidović, Mater. Sci. Forum **518**, 331 (2006).