Configuration-interaction relativistic-many-body-perturbation-theory calculations of photoionization cross sections from quasicontinuum oscillator strengths

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CI-RMBPT calculations of photoionization cross sections from quasi-continuum oscillator strengths

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(Dated: November 24, 2014)

Many applications are in need of accurate photoionization cross-sections, especially in the case of complex atoms. Configuration-interaction relativistic many-body theory (CI-RMBPT) that has been successful in predicting atomic energies, matrix elements between discrete states, and other properties is quite promising, but it has not been applied to photo-ionization problems owing to extra complications arising from continuum states. In this paper a method that will allow the conversion of discrete CI-(R)MPBT oscillator strengths (OS) to photo-ionization cross sections with minimal modifications of the codes is introduced and CI-RMBPT cross sections of Ne, Ar, Kr, Xe are calculated. A consistent agreement with experiment is found. RMBPT corrections are particularly significant for Ar, Kr, and Xe and improve agreement with experiment compared to the particle-hole CI method. The demonstrated conversion method can be applied to CI-RMBPT photo-ionization calculations for a large number of multi-valence atoms and ions.

PACS numbers: 32.80.Fb, 31.10.+z, 31.15.A-, 31.30.Jv

Many applications, such as plasma modeling and opacity calculations, are in need of accurate photoionization cross-sections, especially in the case of complex atoms. Fairly simple approaches, such as random-phase approximation (RPA), have been applied to calculations of photo-ionization cross-sections in alkali-metal [1] and noble-gas atoms [2], but they are not adequate for an arbitrary atom. A more general R-matrix approach has been used, but owing to the complexity of implementation, it is not easy to incorporate into existing precision atomic-structure methods to systematically improve accuracy. Configuration-interaction relativistic many-body theory (CI-RMBPT) formalism that has been successful in predicting energies, matrix elements, and other properties of bound states of atoms [3–6] is quite promising, but it has not applied to photo-ionization problems owing to extra complications arising from continuum states. In this letter a method is introduced to convert discrete CI-(R)MPBT oscillator strengths (OS) to photo-ionization cross sections with minimal modifications of the codes and CI-RMBPT cross sections are computed.

The proposed conversion method is the generalization of the previous approach given in Ref.[7] that consisted of placing an atom in a cavity, calculating oscillator strenghts f_i to quasi-continuum states, and converting them to the differential cross section $\sigma(\epsilon)$ using the relation:

$$\sigma(\epsilon) = 4.03 \times 10^{-18} \frac{df(\epsilon)}{d\epsilon}. \tag{1}$$

The derivative was determined from discrete energies of quasi-continuum states ϵ_i, also available in the calculations,

$$\frac{df(\epsilon)}{d\epsilon} \approx \frac{2f_i}{\epsilon_{i+1} - \epsilon_{i-1}}. \tag{2}$$

The derivative can be calculated quite accurately using Eq.(2) for monovalent atoms, but large uncertainty appears in multi-valence atoms. This is the main difficulty for the conversion. Fortunately with the specific statistical averaging over multiple configurations to be described here fairly accurate cross sections still can be obtained.

It is notable that a cavity is also used in R-matrix methods [8]; however, many important differences exist [9] between the methods. In particular, the method presented here does not require modifications of the CI-(R)MBPT codes, while the R-matrix approach would lead to significant changes, which would be quite very difficult to make in CI-MBPT programs considering the complexity of the codes developed for multi-valence atoms [3]. The advantage of the R-matrix approach, on the other hand, is that the conversion procedure described here is not required since continuum wavefunctions are properly normalized. If the R-matrix approach were properly incorporated into the CI-MBPT formalism, better accuracy could be achieved. The current work can be considered as the first step for the development of the R-matrix CI-MBPT method.

We illustrate the accuracy of the method proposed here on the example of CI-RMBPT calculations of cross sections of Ne, Ar, Kr, and Xe. These atoms are chosen for the following reasons: 1) noble-gas atom photoionization cross sections have been measured with high precision; 2) the number of particle-hole configurations is relatively small, facilitating the investigation of the effects of various parameters on the accuracy; 3) an accurate particle-hole CI+MBPT method has been previously developed for these atoms with agreement demonstrated for energies, oscillator strengths, and g-factors [6]; 4) these atoms are of considerable interest for applications.

In current calculations, we use the particle-hole (PH) CI-RMPBT method described previously [6]. The CI-RMBPT terms are evaluated using radial B-spline basis sets. To generate the basis functions for calculations of photo-ionization cross-sections, the following steps were implemented. First, the Dirac-Hartree-Fock (DHF) potential was generated for a closed-shell atom, such as Ne, Ar, Kr, and Xe. Next, a B-spline subroutine was used to obtain basis sets for the core and virtual states in the frozen DHF ground-state potential. The spherical cavity "bag" boundary condition $P(R) = Q(R)$, where $P(r)$ and $Q(r)$ are the large and small components of the radial Dirac wave function, was imposed to make this basis discrete. The basis consisted of 40-100 radial functions for each spin-orbit index, with the maximum orbital angular momentum restricted to 5. The continuum wavefunctions were replaced with quasicontinuum orbitals. Only minimal modifications were made of existing CI-RMBPT codes and auxiliary subroutines, including the B-spline subroutine. Namely, the maximum number of spline functions was increased from 40 to 100, to improve numerical accuracy, which was estimated from comparison of results when both the number of splines and the cavity size were varied.

Particle-hole interactions in noble-gas atoms are strong and have to be treated in all orders using the CI approach [5]. For this, the PH state functions

$$\Phi_{JM}(av) = \sum_{m_a m_v} (-1)^{j_v - m_v} (2J+1)^{1/2} \begin{pmatrix} j_v & J & j_a \\ -m_v & M & m_a \end{pmatrix} \times a_{vm_v}^\dagger a_{am_a} \tag{3}$$

are introduced for the construction of the CI matrix $H[a'v'(J), av(J)]$. Here J is the total coupled angular momentum, M is its projection, j_v and m_v are the angular momentum and its projection of the excited state v, j_a and m_a are the angular momentum and its projection of the hole state. The effective Hamiltonian, which in the case of CI-RMBPT contains RMBPT corrections, is evaluated between PH state functions and diagonalized to obtain the expansion coefficients of the coupled excited states of noble-gas atoms. It is known that the particle-hole CI approach, restricted to single excitations, does not provide very high accuracy, and it is necessary to take into account particle-core and hole-core interactions. In principle the CI basis can be extended to include double and triple excitations, but the basis becomes large. Alternatively, following the CI-MBPT method, MBPT corrections are incorporated to account for most important interactions beyond the single-excitation CI. We include second-order effects and some important higher-order effects by modifying energies in the denominators. Such an approach has been successful for predicting a large number of excited states and transitions [5, 6].

The quasi-continuum PH spectrum generated in CI-(R)MBPT or CI calculations is quite irregular and the cross section calculated with Eqs. (1-2) has poor accuracy. Even averaging over a large number of points does not solve the problem, leading to the loss of resolution on the energy scale. Below we will demonstrate an alternative method of calculations of the cross section based on the fitting of the sums of oscillator strengths and the differentiation of the fitted curve.

The rationale for this approach is the following. If the differential cross section is integrated over energy, it becomes related (compare Eq.(1)) to the sums of discrete quasi-continuum OSs

$$I(E_i) = \int_{E_0}^{E_i} \sigma(E) dE \approx F_i \equiv 4.03 \sum_{j \le i} f_j + C \tag{4}$$

(Here, C is the constant accounting for the contribution of bound discrete states, E_0 is the ionization energy, the photoionization cross section is in Mb units.) Because now there is no division by energy intervals, the accuracy of theoretical results not affected by the irregularity of energy level is expected adequate as it is illustrated for Ne (Fig. 1). (Note that a substantial difference exists between two fairly reliable Ne experimental measurements [10] and [11]. We chose the former, since the precision claimed there is 1-3%, higher than in the latter, 5%, estimated for the method in the follow up publication [12].) The method of comparison of the integrated cross sections and the sums of quasi-continuum OSs can already be useful in its own right for tests of theory and experimental results; however, it is also possible to convert the sums to differential cross section. Now of course energy intervals will reappear in the problem, and we have to find a way to reduce "noise." Differentiation of noisy data is an ill-posed problem in general, but it is well-known that smoothing can dramatically improve accuracy. By comparing cross sections obtained by the differentiation of various polynomial fittings of data subsets, we found that the line fitting method is sufficiently accurate. Thus this method is chosen in our final calculations, with the advantage of simple analytical solution. In this case the cross section at the energy E_l is:

$$\sigma(E_l) = \frac{(2N+1) \sum_{i=l-N}^{l+N} E_i F_i - \sum_{i=l-N}^{l+N} E_i \sum_{i=l-N}^{l+N} F_i}{(2N+1) \sum_{i=l-N}^{l+N} E_i^2 - (\sum_{i=l-N}^{l+N} E_i)^2} \tag{5}$$

where E_i is the energy of the ith quasicontinuum state, and summation is carried out symmetrically around $i = l$. The number of averaging points $2N + 1$ is optimized to reduce errors without reducing significantly resolution on the energy scale for a smooth distribution. A typical optimal value is 41 for all noble gas atoms. Although we will illustrate the accuracy of the method with quite specific atoms, the method can be used for obtaining differential cross section distributions from quasi-continuum discrete OSs more generally: for complex atoms and molecules and for theories other than CI-RMBPT.
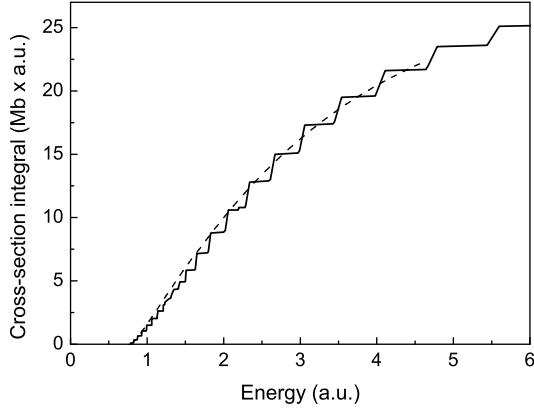
FIG. 1: Comparison for neon of the integrated experimental photoionization cross section of [10] (dashed line) with the sum of quasicontinuum CI+RMBPT values (solid line)
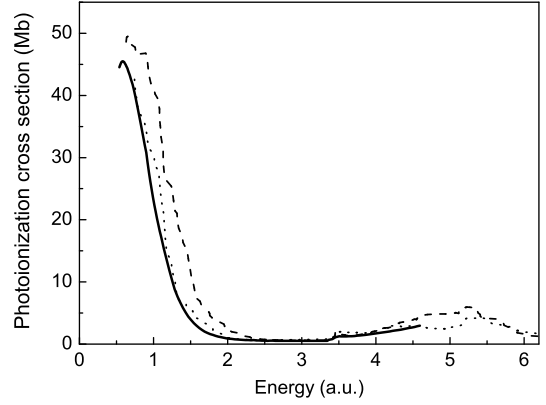

FIG. 3: Krphotoionization cross sections: the solid line - expt.[10], the dotted line - CI+RMBPT, the dashed line - CI calculations
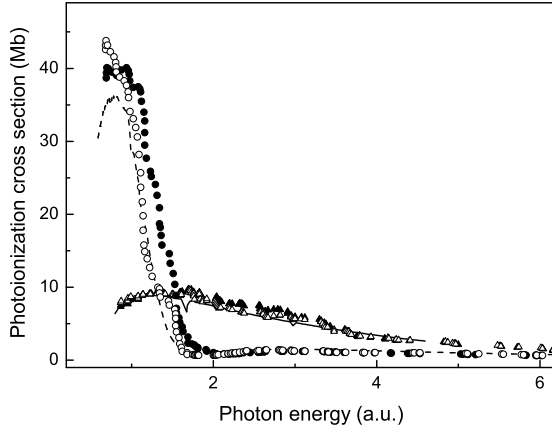

FIG. 2: Ne and Ar photoionization cross sections. Ne data are under 10 Mb: solid line - expt.[10], open triangles - CI+RMBPT, solid triangles - CI. Ar data: dashed line - expt.[12], open circles - CI+RMBPT, solid circles - CI

FIG. 4: Xe photoionization cross sections: the solid line - Xe expt.[10]; the stars - Xe CI+RMBPT, the open circles - Xe CI.

In order to test the accuracy of the current photo-ionization theory and conversion method, we calculated CI-RMPBT photo-ionization cross sections for noble gas atoms from Ne to Xe and compared them with experiment. In addition we present CI calculations to evaluate the contribution from RMBPT part and estimate theoretical accuracy. The oscillator strengths from the ground state to the quasicontinuum states were converted to photo-ionization cross sections by using line-fitting method and differentiation, as described in the previous section. The number of data points for line fitting was chosen to minimize "noise" without substantial reduction in resolution on the energy scale. This number depends on the distance between quasicontinuum levels and hence the cavity size.
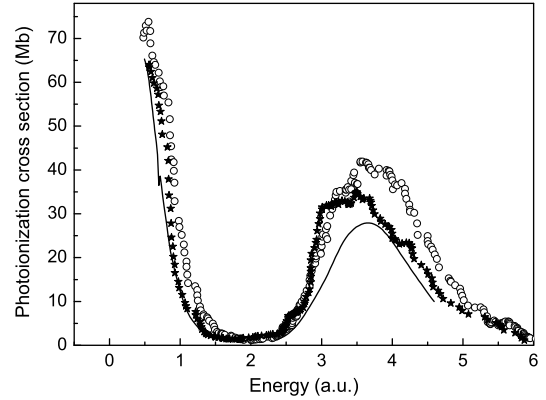
The results for neon are shown in Fig. 2 (the data below 10 Mb). The PI cross section calculated with the CI-RMBPT method, expected to be accurate in neon, agrees well with experiment for the whole range of experimental energies. The CI results agree with experiment as well, but CI-RMBPT values appear to be closer to the experimental cross section. By extrapolating the difference between CI-RMBPT and CI results, which is due to RMBPT correction, it is possible to estimate theoretically that the CI-RMBPT calculation accuracy is on the order of a few percent. Some "fluctuations" of similar order in theoretical calculations are present due to the conversion of discrete OSs into cross sections. These fluctuations can be further reduced by additional smoothing, but this reduces energy resolution.

In Fig. 2, a comparison of CI+MBPT, CI, and experimental cross sections is shown also for argon. The

case of argon reveals much better agreement of the experiment with the CI+MBPT than with the CI theory, especially on the steep slope, with the agreement being equally good at energies above 2 a.u. Substantial deviation of both theories from experiment is observed at 1 a.u. energy, which can be attributed to both inaccuracy of the conversion procedure and neglected RMBPT terms. At the steep slope, the RMBPT contribution leads to a shift of the curve to the left by about 0.2 a.u. The shift due to neglected higher-order effects is expected to be smaller, so we can conservatively state that the horizontal error is about 0.1 a.u. The vertical error is about 5 Mb on the slope. The conversion errors are smaller in this case than the error due to neglect RMBPT terms.

In the case of Kr (Fig.3), the accuracy of CI+MBPT results is similarly better than that of the CI results on the whole range of shown energies. The RMBPT corrections in Kr resulting in the energy shift of the PI curve have somewhat increased as expected for the sequence and are clearly needed to be included. Finally the Xe cross sections (Fig.4) also follow the trends of Ar and Kr that the slope portion of the differential cross section is much better reproduced with the CI-RMBPT than with the CI theory. However, the RMBPT shift becomes smaller than in Ar and Kr. On the other hand, the Xe cross section has a well pronounced second peak, which although is still better reproduced with the CI-RMBPT than CI calculations, reveals noticeable discrepancy between theory and experiment. This discrepancy might be attributed to omitted higher-order RMBPT effects.In general the theoretical accuracy can be roughly estimated as the difference between CI and CI-RMPBT values, so the presented calculations not only give more accurate values than the simpler CI calculations but also theoretical errors.

It is interesting to compare the current results with theoretical results reported in the literature. A detailed comparison of previous theories such as RRPA, Hartree-Fock(HF), and R-matrix is given in Ref.[2]. For total PI cross section, it has been shown that the RRPA of Ref.[2] performs well in neon, similarly as our CI and CI-MBPT, which is not surprising considering small difference in results between CI and CI-MBPT. It is, however, more surprising that RRPA of Johnson and Cheng agree well with theory in Ar, while we found that CI cross section is shifted with respect to experimental values. At the peak, RRPA, CI, and CI-MBPT all give higher values than experiment. The tail behavior is again quite similar for CI-MBPT, CI and RRPA. In Kr, the RRPA values deviate significantly from experiment, while CI-MBPT gives very close agreement. This is one case where CI-MPBT shows clearly the advantage over the previous theories. Finally, Xe CI-MBPT, CI and RRPA agree. In general it can be concluded that CI-MBPT performs better for total PI than RRPA and especially HF (the length or velocity forms) theories analyzed in Ref.[2] consistently for the considered atoms. R-matrix calculations [13] have been compared in Ref.[2] for partial cross sections. The performance of the R-matrix approach was better than that of RRPA in Neon, but worse in Ar. So it appears that R-matrix method is not necessary better than RRPA. However, when looking at R-matrix results it is important to understand the approximations used, since the complexity of the approach requires some practical constrains on the basis sets. Our approach, unlike R-matrix methodology, facilitates incorporating much more complicated CI-MBPT corrections, and this can be considered its main advantage.

From the given demonstrations, we can summarize that the CI+RMBPT theory gives higher accuracy than CI for noble-gas atoms from Ne to Xe. This is quite an encouraging result, which not only confirms that the CI+RMBPT method is an accurate theory of atomic properties in the considered energy range, but also that the conversion procedure described here can be used for accurate cross section calculations. The developed method can be applied to many complex atom where multiple irregular levels exist in the quasi-continuum spectrum. In particular, the CI-RMBPT quasi-discrete OSs can be converted to cross sections in many atoms.

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