A simple method for obtaining electron scattering phase shifts from energies of an atom in a cavity

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We present a simple method for obtaining elastic scattering phase shifts and cross sections from energies of atoms or ions in cavities. This method does not require calculations of wavefunctions of continuum states, is very general, and is extremely convenient from practical point of view: some conventional computer codes designed for the energies of bound states can be used without modifications. The application of the method is illustrated on an example of electron scattering from Kr and Ar. From Brueckner orbital energies in variable cavities, we have obtained ab initio cross sections that are in close agreement with experiment. The relativistic effects are also considered and found to be small below 10 eV.

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Conventional methods of calculations of scattering cross sections are cumbersome, inconvenient, and very often inaccurate. This is only because they all are based on computing continuum, or sometimes quasicontinuum, wavefunctions and asymptotic fittings to extract phase shifts. Such an approach requires modifications of conventional atomic structure codes, developed for bound states, or just writing new programs altogether. For a known potential it is not a difficult task – this is why numerous semi-empirical calculations can be found in the literature – but the level of accuracy and theoretical uncertainty of calculations based on ad hoc potentials can not be totally satisfactory. For ab initio calculations already complicated codes have to be rewritten, which takes considerable amount of time. For multi-configuration Hartree-Fock (MCHF) method this was undertaken by Saha [1, 2] to obtain ab initio results in agreement with experiment. However, many-body perturbation theory (MBPT) methods, which were developed for fundamental symmetry tests, have not been used for calculations of electron scattering cross sections.

The method we propose in this letter is very simple and general: instead of finding continuum wavefunctions and fitting them to asymptotical solutions to obtain phase shifts for given electron energies, we impose a boundary condition on an atom, an ion, or a molecule to make the spectrum discreet and then from discreet energies extract phase shifts which are uniquely related to these energies. Thus the problem of phase shifts is converted into a conventional problem of finding energies of bound states. Especially simple relation exists, as we will show, in the case of an atom in a spherical cavity.

It can be shown that continuum and quasicontinuum wavefunctions are equivalent. For example, in Ref. [3] it was stated that B-spline solutions obtained in a cavity can be interpreted as a representation of true continuum states with a different normalization, and the energy of the quasicontinuum states can be set to an arbitrary positive value by adjusting the size of the cavity. There are also other methods that give B-spline continuum wavefunctions at any energy: the Galerkin method [4], least-squares approach [5, 6], and free boundary condition approach [7]. The emphasis in these works is placed on applications of B-splines which are very often bundled with the cavity boundary conditions: for the method proposed here, however, the boundary conditions are more essential than B-splines, which are still convenient for evaluation of radial integrals in high-precision MBPT calculations [8].

While our method can be justified mathematically in quite general assumptions, it is not yet obvious that the method will be accurate in practical calculations, so we will illustrate the usefulness and accuracy of the method on specific examples such as the MBPT calculations of electron elastic scattering phase shifts and cross sections from Ar and Kr. The MBPT is chosen because it can provide the best accuracy for a negative mono-valent ion, e.g. Ar\(^{−}\), uses cavity-bound basis functions, so the code does not need modification, and allows systematic consideration of correlations. To obtain correct electron-noble gas scattering cross sections it is necessary to include the direct and exchange potentials from a frozen noble-gas atom as well as core polarization effects. The direct part of the unperturbed atomic potential produces a phase shift opposite to that of the exchange part. The combined phase shift from the frozen atom is opposite in sign to that of the core-polarization. We will show that so-called Brueckner-orbital (BO) approximation treats accurately these effects and results in good precision. The accuracy can be further improved by using all-order couple-cluster method, or other accurate methods developed for mono-valent atoms. The calculations of phase shifts from energies for other systems should be also possible and will be undertaken in future.

Apart from illustration purpose, the calculations will serve to provide accurate ab initio cross sections for comparison with other theories and experiments and to improve understanding of this particular system. Despite longer than a century history [9] that experiments on electron interaction with gases have, many questions remain open and this area of research is still very active. Elastic scattering of electrons on noble-gas atoms is of
particular interest since many precise measurements are available providing tests for theories which all with a few exceptions are not of ab initio type and are based on pseudopotentials to take into account exchange interaction and significant polarizability of noble-gas atoms by an electron. Although elaborate complicated semi-empirical effective potentials have been developed to achieve good accuracy of calculations, many different calculations and measurements are still in disagreement, and there is clearly significant uncertainty in theoretical understanding. This situation exist in almost all noble-gas atoms.

For example, motivated by uncertainty in cross sections at low energies, which are important for extraction of scattering lengths, first ab initio calculations of low-energy electron scattering from neon [1] and argon [2] based on MCHF method to account for polarization effects have been reported, and good agreement with experiment has been demonstrated. Although MCHF method is very effective in general for the consideration of complicated open-shell ions, in monovalent atoms and low-charge ions this method has lower accuracy than MBPT methods, which were not applied to calculations of electron scattering from noble-gas atoms, probably due to complications associated with continuum states.

With the aid of partial wave expansion,

$$\Psi(r) = \sum_{lm} Y_{lm}^m(\theta, \phi) \frac{P_l(r)}{r}$$

(1)

a total elastic cross section $\sigma_t$ can be found from phase shifts $\delta_l$

$$\sigma_t = \frac{4\pi}{k^2} \sum (2l + 1) \sin^2 \delta_l$$

(2)

which are normally extracted from asymptotic behavior of radial wavefunctions $P_l(r)$ obtained by numerical solution of radial Schrödinger equation

$$\frac{d^2 P_l(r)}{dr^2} + \left[ k^2 - U(r) - \frac{l(l + 1)}{r^2} \right] P_l(r) = 0$$

(3)

for a given energy $E = k^2/2$ as a parameter. In this equation $U(r)$ is some effective potential which describes approximately direct and exchange interaction as well as the attraction due to core polarizability. (Atomic units are used in all equations.) The radial wavefunctions can be also obtained by using ab intio atomic structure methods such as MCHF [1,2] or MBPT. Because wavefunctions are not always available in precision MBPT calculations and most codes output either energies or matrix elements, the extraction of phase shifts from wavefunctions is not very convenient. However, it is not necessary: phase shifts can be obtained from energies of an atom bound to a cavity, which is a natural setting in MBPT calculations. The extraction is possible because the cavity uniquely encodes phase shift information into energies of quasicontinuum states and quasicontinuum wavefunctions are proportional to true continuum wavefunctions if their energies are the same. The last statement can be easily proved since the continuum and quasicontinuum wavefunctions are both unique solutions of the radial differential equation with the same boundary condition at $r \to 0$, the same energies, although with different normalization conditions and maybe sign convention. The equivalence of quasicontinuum and continuum states was also stated in Ref. [3]. At large $r$ continuum and quasicontinuum solutions approach asymptotically the solution in empty cavity proportional to $r j_l(r)$, where $j_l(r)$ are spherical Bessel functions, and the effect of the atomic potential is only in phase shifts which can be determined from the asymptotic form of the wavefunctions or from energies for a known cavity radius $R$, which is our proposed method:

$$\delta_l(E_n) = x_{ln} - \sqrt{2E_nR}$$

(4)

where $x_{ln}$ is the $n^{th}$ zero of the spherical Bessel function $j_l(x)$. Accurate values of $x_{ln}$ can be found in mathematical reference books, for example on page 467 of Ref. [10], column $j_{v,s}$ where $v = l + 1/2$ and $s = n$. For $l = 0$, $x_{0n} = n\pi$. The lowest quasicontinuum state of a given symmetry has to be used with the first zero of the corresponding spherical Bessel function, the next state with the second zero, etc.

Energies of quasicontinuum states are calculated in Brueckner-orbital approximation, which accounts for core-polarization effects with relatively high precision. First, the Dirack-Hartree-Fock (DHF) equation is solved for a closed-shell atom (Ar or Kr). Then in the obtained DHF potential, B-spline finite basis is generated. In this basis, the Hamiltonian matrix $h_{ij} = \delta_{ij}\epsilon_i + \Sigma_{ij}(\epsilon_0)$,

$$\Sigma_{ij}(\epsilon_0) = \sum_{kcmn} \frac{(-1)^{j_m+j_n-j_i-j_c} X_k(icmn)Z_k(mnjc)}{(2j_i+1)(2k+1)} \epsilon_0 + \epsilon_c - \epsilon_m - \epsilon_n + \sum_{kbcn} \frac{(-1)^{j_c+j_n-j_b-j_c} X_k(icmn)Z_k(mnjc)}{(2j_i+1)(2k+1)} \epsilon_0 + \epsilon_n - \epsilon_b - \epsilon_c$$

(5)

is calculated and diagonalized to obtain BO energies. The summation runs over core states $c$, excited states $n, m$, and angular momenta $k$; the matrix elements are calculated between all possible states $i$ and $j$. The coupled radial integrals $X_k(abed)$ and $Z_k(abed)$ are defined for example in [11]. The self-energy matrix elements $\Sigma_{ij}(\epsilon_0)$, which take into account dominant part of core-polarization effects, depend on electron energy $\epsilon_0$ and contains non-local interaction, so that they can not be approximated accurately with a single effective potential unless the energy range is small, $\epsilon \leq \epsilon_0$, and the distance between electron and an atom is large compared to the size of the atom so that exchange interaction can be neglected. The diagonalization is important because energy differences between quasi-continuum states are small. Essentially, all-order methods are necessary, at least to include chained self-energy corrections. Pure 2nd- or 3rd-order expansions will be inaccurate due to this reason, and we will illustrate this numerically for
TABLE I: “Bag” model artifact. An extra phase shift \( \delta \) due to the “bag” boundary condition for an empty cavity of \( R=15 \) a.u. is compared with prediction \( \alpha \sqrt{E/2} \) in the Pauli approximation; \( l \) is the angular momentum of the state, \( n \) is the radial quantum number.

| \( l \) | \( n \) | \( E_{\text{cav}} \) | \( \delta \) | \( \alpha \sqrt{E/2} \) |
|-------|------|----------------|--------|----------------|
| 1     | 1    | 4.48[-2]       | 1.10[-3]| 1.09[-3]      |
| 3     | 2    | 2.64[-1]       | 2.69[-3]| 2.65[-3]      |
| 4     | 3    | 4.39[-1]       | 3.80[-3]| 3.42[-3]      |
| 2     | 1    | 7.38[-2]       | 1.41[-3]| 1.40[-3]      |

2nd-order MBPT in the next section, but couple-cluster methods, which treat some diagrams in all orders, are expected to give good accuracy. The simplest future improvement for the current BO theory is to take into account screening, which is more significant in heavier noble-gas atoms.

Relativistic effects can be also carefully considered, if necessary. One effect is the difference in energies between for example \( p_{1/2} \) and \( p_{3/2} \) states, which for low-energy scattering is small, but becomes more pronounced at higher energies. The self-energy correction is also slightly different in non-relativistic and relativistic cases because intermediate states in the summation are different. One interesting consequence of the use of relativistic basis in calculations is that the boundary condition is not \( P(R) = 0 \), but rather \( P(R) = Q(R) \), where \( P(r) \) and \( Q(r) \) are large and small components of the radial Dirac wavefunction. This is so-call “bag” boundary condition which is required to avoid Klein paradox \( ^{12} \) and spurious solutions observed in Ref. \( ^{13} \). Using the Pauli expansion, it can be shown that the difference in boundary conditions produces additional phase shift equal to \( \alpha \sqrt{E/2} \), where \( \alpha \) is the fine-structure constant and \( E \) is the energy of the electron. This shift can be obtained if we compare energies generated in the empty cavity with energies expected from the zeros of the spherical Bessel functions as illustrated in Table I. Apparently, the Pauli approximation explains well and predicts accurately the “bag” shift as long as \( \alpha \sqrt{E/2} \ll 1 \). When the shift is large, it is necessary to subtract it or even to reanalyze this method more carefully. In the calculations presented below the energies were small enough to neglect this effect as well as some other relativistic effects.

The results of our calculations for elastic cross section on argon is shown in Fig. 1. Close agreement with experimental data is achieved in the range below 10 eV if the self-energy chain corrections are included (BO energies are used) and the cross sections from partial waves with \( l = 0 - 2 \) are added. To emphasize the importance of \( l > 0 \) contributions in Fig. 1 we also plot \( s \)-wave cross section separately and in Fig 2 we compare phase shifts from \( s-, p- \), and \( d \)-waves. To check that our predictions for phase shifts are correct, we compare them with experimental phase shifts. Contributions from higher order partial waves are much smaller, but can be in principle included. At low energies, the dominant contribution comes from \( s \)-waves, which is expected; however, at energy about 0.36 eV, \( s \)-wave \( \sin \delta \) crosses zero, resulting in a minimum of the cross section. In this region the \( p \)-wave and \( d \)-wave contributions become particularly important and affect the shape of the Ramsauer-Townsend minimum.

Although the diagonalization does not change much energies of the quasi-continuum states, the phase shifts and cross sections obtained from energies before (dotted line) and after (solid line) diagonalization are quite different, see Fig 1. The agreement is achieved only in the last case. In the case when argon cross section is calculated from DHF energies and thus polarization effects are ignored, the cross section is completely inaccurate.
At low energy DHF scattering length is exactly opposite to correct value. DHF potential cross section does not depend much on energy and this potential in the range below 3 eV can be approximated by an infinite potential at $R < R_0$, where $R_0 = 1.42 - 1.53$ a.u. approximately equal to the size of the argon electron cloud about 1.56 a.u. Simple interpretation of this is the repulsion due to Pauli exclusion principle.

Because the experiments at very low energy are difficult, we also find scattering length by extrapolating our results to zero energy, $R_{\text{scatt}} = -1.47 \pm 0.03$ a.u. There are several other calculations of the argon scattering length: -1.63 a.u. by Asaf et al. \cite{17}, from studies of perturbed optical absorption in gases, -1.492 by Buckman and Lohmann \cite{15} from TSC studies, and -1.486 by Saha \cite{21} from low energy calculations. Our value disagrees only with the value from Ref. \cite{17}.

Our theoretical cross section for krypton is shown in Fig. 3. The agreement with the cross section obtained by Plenkiewicz et al. \cite{19} from a pseudopotential is very close. The agreement with experiment is also relatively good in all range of energies shown, although some disagreement can be seen near the cross-section minimum, which can be due to the inaccuracy of both theory and experiment.

In this paper, we proposed a simple method for calculations of phase shifts from energies of quasicontinuum states and illustrated its high precision with MBPT calculations. The method in general can be applied to many scattering problems: electron scattering on various atoms and ions, positron scattering, atom-atom scattering; however, in each case some specific atomic structure method has to be developed to achieve practical precision. Discussed BO approximation can be used only for electron scattering on closed-shell atoms and ions.

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