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 precise *ab initio* many-body perturbation theory energies of atoms in variable cavities. This method does not require calculations of wave functions of continuum states, can be generalized to many atoms and ions, and is extremely convenient because existing codes developed for energy calculations can be used without modification. The high precision of the method and close agreement with experiment are illustrated on examples of *e*-Ar and *e*-Kr scattering. Correlations as well as relativistic corrections are systematically considered.

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Problems involving continuum states, which are encountered across many fields, including atomic, nuclear, molecular, and condensed-matter physics, and in a variety of processes, such as scattering, photoionization, and impact excitation, are often more difficult theoretically than those involving discrete states. Because both types of states are solutions of the same Schrödinger equation, it should be possible to include correlations at the same level. A substantial obstacle for equal treatment is the difference in boundary conditions, so in this Letter we explore the possibility of using the same boundary conditions. Moreover, we propose a method that reduces the electron-scattering problem to the problem of the discrete energies, which can be accurately calculated using available computer codes. Apart from the academic interest (where some textbooks can benefit from its simplicity), this method can be of great practical interest. As will be demonstrated in this Letter, it opens possibilities for accurate *ab initio* calculations of scattering cross sections. Below, several nontrivial issues related to continuum problems will be addressed: (1) continuum problems can be accurately treated using quasicontinuum states; (2) a desirable energy range can be covered by variations of cavity radii; (3) the solution of the elastic scattering problem can be reduced to the calculations of discrete energies; (4) correlation effects can be accurately accounted for with *ab initio* methods. Although some ideas apply to a broad range of continuum problems, we will concentrate on the elastic scattering cross sections that have been accurately measured.

Conventional methods based on continuum wave functions or R matrices [1] are not convenient for implementation with many-body perturbation theory (MBPT) [2], large-scale configuration interaction (CI) [3], multiconfiguration Hartree-Fock (MCHF) [4], CI + MBPT [5,6], and other accurate *ab initio* methods for atoms and ions with strong correlations. The main reason is that complicated existing codes have to be rewritten. For the MCHF method this was done by Saha [7,8] to obtain *ab initio* elastic scattering cross sections in agreement with experiment. The CIV3 code, which resembles small-scale MCHF, was used in R matrix calculations by Fon *et al.* [9,10]. *Ab initio* MBPT methods were also applied [11,12].

In this Letter we propose and investigate a simple approach in which, by introducing a spherical cavity and imposing specific boundary conditions at its radius, we convert an electron-scattering problem into the problem of finding discrete energies, which can be readily calculated with available codes developed for bound states. There is some similarity with the R-matrix method, which also introduces artificial boundary conditions, but the method proposed here differs in many respects, is simpler, and completely avoids modifications of atomic-structure codes: (i) at the cavity radius, atomic and scattering electron's wave functions are set to zero in the nonrelativistic case, or the large component is set equal to the small component in the relativistic case—the R-matrix method deals with arbitrary values and derivatives at the boundary; (ii) the region outside the cavity, which in the R-matrix approach is necessary for computing S and K matrices, is not needed; (iii) the Bloch L operator [13] is absent; (iv) the cavity size is varied to scan scattering energies, while in the R-matrix method it is fixed. As a result, in our method standard numerical routines used to generate Hartree-Fock (HF) or Dirac-HF (DHF) potentials, B-spline HF/DHF basis functions, and to calculate MBPT energies can be applied immediately.

Continuum and quasicontinuum wave functions are equivalent. For example, in Ref. [14] it was stated that B-spline solutions obtained in a cavity can be interpreted as a representation of true continuum states with 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 wave functions at any energy: the Galerkin method [15], the least squares approach [16,17], and the free boundary condition approach [18]. 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 [19].

While the proposed method can be justified mathematically in quite general assumptions, it is not yet obvious that it will be accurate in practical calculations, so we will illustrate the usefulness and accuracy of the method on specific examples of calculations of e-Ar and e-Kr elastic scattering phase shifts and cross sections. Energies of Ar^- and Kr^- ions in cavities for extraction of phase shifts will be obtained using a set of MBPT subroutines. The MBPT method provides sufficient accuracy for these ions and allows systematic consideration of correlations; in addition, B-spline cavity-bound basis functions, used for evaluation of MBPT terms, automatically impose necessary boundary conditions. To obtain correct elastic scattering cross sections it is essential to include effects beyond HF approximation due to strong cancellations. The Brueckner-orbital (BO) approximation, defined in Ref. [2] and also referred to as the quasiparticle-orbital approximation in Refs. [12,20], accurately treats these effects and results with good precision. The accuracy can be further improved with some other more accurate methods developed for monovalent atoms. The calculations of phase shifts from energies for other systems should also be possible and will be undertaken in the future.

Apart from illustration purposes, 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. In spite of the fact that the history of experiments on electrons interacting with gases is longer than a century [21], 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, with a few exceptions, are not all of the *ab initio* type and are based on pseudopotentials. Although elaborate complicated semi-empirical effective potentials have been developed to achieve good accuracy, many 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.

The method.—In general the partial wave expansion

$$\Psi(\mathbf{r}) = \sum_{lm} Y_l^m(\theta, \phi) \frac{P_l(r)}{r} \tag{1}$$

allows one to relate total elastic cross sections σ_t,

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

to phase shifts δ_l, so the main problem is to find phase shifts. By definition, they can be extracted from asymptotic behavior of radial wave functions $P_l(r)$ of a scattered electron. The wave functions can be obtained by numerical solution of the Schrödinger equation for a given energy $E = k^2/2$ as a parameter by using *ab initio* atomic-structure methods such as MCHF [7,8] or MBPT [12]. Because wave functions are not always available in precision calculations and most codes output either energies or matrix elements, the extraction of phase shifts from wave functions is not very convenient. In our method phase shifts are obtained from energies of an atom bound in a cavity, which is a natural setting in MBPT calculations. The extraction is possible because the cavity uniquely encodes phase shift information into the energies of quasicontinuum states, and quasicontinuum wave functions are identical to true continuum wave functions if their energies are the same. The last statement can easily be proven since the continuum and quasicontinuum wave functions 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. [14], and we would like to note in passing that not only scattering but also many other problems can be simplified and solved by replacing continuum with quasicontinuum wave functions. At large r, continuum and quasicontinuum solutions approach asymptotically the solution in an empty cavity proportional to $r j_l(kr)$, where $j_l(x)$ are spherical Bessel functions and $k = \sqrt{2E}$, and the effect of the interaction with an atom is given only in phase shifts. The phase shifts can be determined from the asymptotic form of the wave functions or from energies for a known cavity radius R as

$$\delta_l(E_n) = x_{ln} - \sqrt{2E_n} R. \tag{3}$$

Here x_{ln} is the nth zero of the spherical Bessel function $j_l(x)$. For a given angular momentum l the lowest quasicontinuum energy has to be used with the first zero of the corresponding spherical Bessel function, the next energy with the second zero, etc. The formal proof of Eq. (3) and its relativistic extension will be presented in a forthcoming paper.

We calculate energies of quasicontinuum states in the Brueckner-orbital approximation, which accounts for the dominating part of the correlation. First, the DHF equation is solved for a closed-shell atom (Ar or Kr). Then, in the obtained DHF potential, the B-spline finite basis is generated. In this basis, the Hamiltonian matrix $h_{ij} = \delta_{ij}\epsilon_i + \Sigma_{ij}(\varepsilon_0)$,

$$\begin{aligned} \Sigma_{ij}(\varepsilon_0) = {} & \sum_{kcmn} \frac{(-1)^{j_m + j_n - j_i - j_c}}{(2j_i + 1)(2k + 1)} \frac{X_k(icmn) Z_k(mnjc)}{\varepsilon_0 + \varepsilon_c - \varepsilon_m - \varepsilon_n} \\ & + \sum_{kbcn} \frac{(-1)^{j_i + j_n - j_b - j_c}}{(2j_i + 1)(2k + 1)} \frac{X_k(icmn) Z_k(mnjc)}{\varepsilon_0 + \varepsilon_n - \varepsilon_b - \varepsilon_c}, \end{aligned} \tag{4}$$

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 $X_k(abcd)$ and $Z_k(abcd)$ are defined, for example, in [22]. The self-energy matrix elements $\Sigma_{ij}(\varepsilon_0)$ depend slowly on electron energy ε_0, which can be chosen to be the energy of the lowest quasicontinuum state. The diagonalization is important because energy differences between quasicontinuum states are small. Because of this, the second-order energy is inaccurate as illustrated below. One possible improvement for the current BO theory is to take into account the screening of the Coulomb interaction by the noble-gas electrons, which is more significant in heavier atoms. Perturbation theory including the screened Coulomb interaction provided an accuracy of 0.1% for Fr energy levels [23].

Relativistic effects can be also carefully considered, if necessary. One such effect is the difference in energies between fine-structure states, which for low-energy scattering is small but becomes more pronounced at higher energies. To avoid the Klein paradox [24] and the spurious solutions observed in Ref. [25], the use of relativistic basis requires so-called "bag" boundary conditions, $P(R) = Q(R)$, where $P(r)$ and $Q(r)$ are large and small components of the radial Dirac wave function. The bag phase shifts can be obtained if we compare energies generated in the empty cavity with energies expected from the zeros of the spherical Bessel functions. At energies $E \ll 2m_e c^2$, the shifts accurately follow the Pauli-expansion equation $\alpha\sqrt{E/2}$, where α is the fine-structure constant. Below 20 eV, relativistic corrections are small. In some applications, such as spin-flipping scattering, the relativistic effects are essential and should be considered in detail, which we would like to do in the future.

Calculations.—The results of our calculations for the e-Ar elastic cross section are shown in Fig. 1. Close agreement with experiment is achieved below 10 eV in the BO approximation after including the partial waves $l \leq 2$. To emphasize the importance of $l > 0$ contributions in Fig. 1 we also plot the BO s-wave cross section separately, and in Fig. 2 we compare BO phase shifts from s, p, and d waves with experiment. Contributions from higher-order partial waves are much smaller and are neglected in this work, 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.

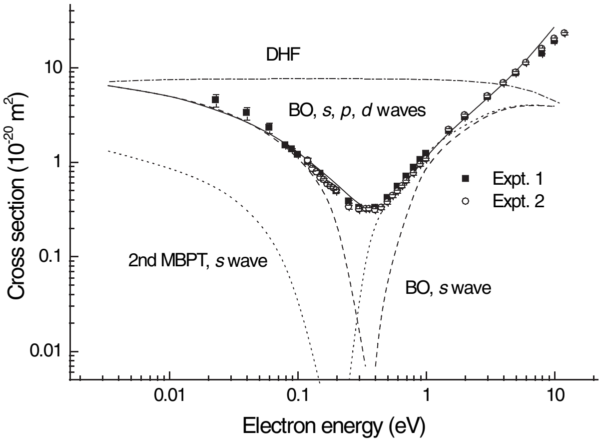

FIG. 1. Low-energy e-Ar cross sections. Comparison of various theoretical approximations with experiment: solid line, BO $l \leq 2$; dashed line, BO s wave; dotted line, second-order MBPT; dash-dotted line, DHF. Experiments: Expt. 1, Ref. [30]; Expt. 2, Ref. [27].

The phase shifts and cross sections obtained from second-order energies, Eq. (4) before diagonalization, and from BO energies, Eq. (4) after diagonalization, are quite different (see Fig. 1), and the agreement is achieved only after diagonalization. Using DHF energies and ignoring excitation effects leads to very inaccurate cross sections. The DHF scattering length is incorrectly positive and independent of energy. This potential can be approximated by a rigid sphere of the size of an argon atom, in accordance with Pauli exclusion principle.

Because experiments at very low energy are difficult, we also find the e-Ar scattering length by extrapolating our results to zero energy, $R_{\text{scatt}} = -1.47 \pm 0.03$ a.u. There are several other calculations: -1.63 [26], -1.492 [27], -1.449 [28], and -1.486 [8]. Our value disagrees only with the value from Ref. [26].

Our theoretical e-Kr cross section is shown in Fig. 3. The agreement with a pseudopotential theory [29] and experiment in the considered energy range is close, although the scatter is larger than in the case of Ar.

In conclusion, we proposed a simple method for calculations of phase shifts from energies of quasicontinuum states and illustrated its high precision with MBPT calcu-

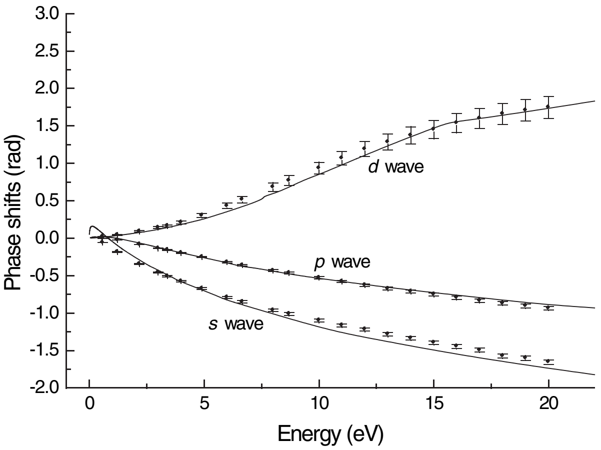

FIG. 2. Comparison of our BO calculations (solid line) with experiment [31] (points with error bars) for phase shifts of electron scattering from argon.

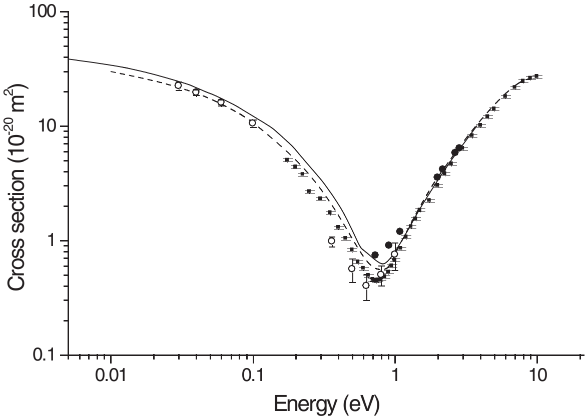

FIG. 3. Low-energy *e*-Kr cross sections. Solid line, our theory; dashed line, pseudopotential calculations [29]. Experiments: open circles with error bars, Ref. [30]; solid circles with error bars, Ref. [32]; solid circles without error bars, Ref. [33].

lations. The method can be extended to many scattering problems: scattering on various atoms and ions, positron scattering, atom-atom scattering, etc.; however, in each case some specific atomic-structure code has to be used to achieve high precision.

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