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LETTER TO THE EDITOR

$^3S^e$ and $^1S^e$ scattering lengths for e^- + Rb, Cs and Fr collisions

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Abstract

We calculate the $^3S^e$ and $^1S^e$ scattering lengths in low-energy e^- + Rb(5s), Cs(6s), and Fr(7s) collisions. Our approach is based on the relativistic version of the modified effective range theory (MERT) and extrapolates eigenphases provided by Dirac *R*-matrix calculations to zero energy. To test the accuracy of our MERT extrapolation method, we compare the fine-structure components for the lowest $^3P^o$ resonance of Fr^- ion with full Dirac *R*-matrix calculations.

Low-energy electron scattering by highly polarizable systems can be described by the modified effective range theory (MERT) whose non-relativistic version has been developed by Fabrikant [1, 2]. This theory assumes that the electron wavelength is large compared to the radius of the *short-range* interaction between the electron and the atom. This is a much weaker restriction than the more common assumption [3] that the electron wavelength is large compared to the radius of the polarization interaction. The non-relativistic version of the MERT method was used to predict the lowest $^3P^o$ resonance states for Rb^- and Cs^- at a few meV above the detachment threshold [2, 4]. Their positions and widths are in good agreement with experimental data for Rb [5] and Cs [6] and accurate relativistic Dirac *R*-matrix calculations (see table 2 in [7]).

The $^3S^e$ and $^1S^e$ scattering lengths in low-energy electron scattering by heavy alkali-metal atoms are known only from non-relativistic calculations [2] for e^- + Rb(5s) and Cs(6s) collisions. No data are available for Fr targets. Recently, Greene *et al* [8] have predicted new trilobite-like states of Rb_2 molecules in a Bose–Einstein condensate. Their model requires accurate scattering length data. Motivated by this work, we have computed accurate $^3S^e$ and $^1S^e$ scattering lengths for e^- + Rb, Cs, and Fr collisions. For this purpose, we have modified the non-relativistic MERT method [1, 2] in order to include relativistic interactions. MERT allows the extrapolation of *ab initio* eigenphases to very low energies. The present MERT uses eigenphases provided by relativistic Dirac *R*-matrix calculations [9] for two particular low scattering energies below the first excitation threshold and extrapolates toward zero energy.

The Dirac *R*-matrix calculations were successfully applied to describe the low-lying spectra of Rb^-, Cs^-, and Fr^- [7, 10] and were found to be in good agreement with various photodetachment and electron scattering experiments on Rb and Cs. Fr is the heaviest alkali-metal atom and, therefore, relativistic interactions (i.e. the spin–orbit coupling) are strong. The study of the low-lying spectra of Fr^- was recently done in calculations of electron–Fr scattering

for energies below 3 eV [7, 10]. These calculations predict a new value for the electron affinity for Fr (0.492 eV) and identify a number of resonances in the low-lying spectra of Fr^-: the $^3P^o$ [7] and $^3F^o$ shape and $^3P^e$, $^1P^o_1$, and $^1D^o_2$ [10] Feshbach resonances below the first excitation threshold.

In this letter we shall first present a modified version of the non-relativistic MERT [2] that includes relativistic effects. Next, the accuracy of the relativistic MERT calculations will be tested by comparing the fine-structure components of the $^3P^o$ resonance for Fr^- with Dirac R-matrix results at the same, very low, scattering energies [7]. Finally, we shall provide $^3S^e$ and $^1S^e$ scattering lengths in e^- + Rb, Cs, and Fr collisions. Throughout this letter we shall use atomic units.

In the non-relativistic version of MERT [2], the scattering phase shift can be written in the following form

$$\tan\delta = -(Mc + d)/(Ma + b) \tag{1}$$

where the coefficients a, b, c, and d depend only on the atomic polarizability (α) and the scattering energy E. These coefficients are calculated from solutions of the Schrödinger equation (including a polarization potential) and can be expressed in terms of Mathieu functions [11, 12]. M, on the other hand, depends on the short-range interaction. It is a meromorphic function of energy and, within the effective range theory (ERT), can be written as

$$M = \beta + \eta E \tag{2}$$

where the parameters β and η can be obtained from *ab initio* phase shifts. If M has a pole in the vicinity of $E = 0$, we use a similar approximation for M^{-1}. In the relativistic case the problem becomes multichannel even below the first excitation threshold because of the admixture of states with different orbital angular momenta and spins. We will now generalize our MERT equations for this case.

At large distances, where the short-range interaction is negligible, the matrix of radial wavefunctions F can be written as

$$F = \phi + \psi K \tag{3}$$

where K is the open-channels block of the reactance matrix, and ϕ and ψ are solution matrices with the following asymptotic form

$$\phi_{ij} \sim \delta_{ij}\sin(kr - l_i\pi/2) \qquad \psi_{ij} \sim \delta_{ij}\cos(kr - l_i\pi/2). \tag{4}$$

The indices i and j designate open channels, and δ_{ij} represents the Kronecker symbol. The solutions ψ and ϕ take into account only the *long-range* polarization interaction which, at low energies, can be represented by a diagonal polarization potential $-\alpha/2r^4$. Therefore, the matrices ψ and ϕ are diagonal in the whole space. They can be expressed in terms of (unphysical) solutions f and g defined by the boundary conditions at the origin. These two pairs of solutions are connected by linear relations

$$\psi(r,k) = f(r,k)a(k) + g(r,k)b(k) \tag{5}$$

$$\phi(r,k) = f(r,k)c(k) + g(r,k)d(k) \tag{6}$$

where all matrices are diagonal. The solutions f and g smoothly depend on energy. As in the one-channel case, all strong energy dependences are contained in coefficients a, b, c, and d. These coefficients are calculated from the non-relativistic Schrödinger equation, as described in [11, 12], since the effects associated with the relativistic dependence of energy on velocity are negligible at low energies. The spin–orbit interaction effects are taken care of by reassigning the scattering channels (J^π classification instead of the ^{2S+1}L classification).

Substituting equations (5) and (6) into (3) and joining F with the internal wavefunction using the matching condition of the R-matrix theory, we find an equation similar to equation (1)

$$K = -(Ma + b)^{-1}(Mc + d). \tag{7}$$

The major difference with the one-channel case is that now a, b, c, and d are diagonal matrices, and $\boldsymbol{M}$ is a non-diagonal matrix (since the short-range interaction is non-diagonal). This increases the number of parameters of the theory. However, the number of parameters can be reduced in a representation where the $\boldsymbol{K}$ matrix is diagonal. This is necessary for computing eigenphases. Let us assume that the matrices a, b, c, and d are not only diagonal but also proportional to the unit matrix. This is valid exactly if we have coupling between channels with the same orbital angular momentum l (e.g. for $J^\pi = 1^-$ scattering when we have coupling between ^{1}P and ^{3}P states). In the case of coupling between different angular momenta (such as for the $J^\pi = 2^-$ and 1^+ scattering symmetries) this assumption is justified by the dominance of the lowest angular momentum at low energies. Higher momenta are suppressed because of the centrifugal barrier. Under this assumption, we apply an orthogonal transformation which diagonalizes the $\boldsymbol{K}$ matrix in equation (7). It is easy to see that the $\boldsymbol{M}$ matrix is also diagonal in the same representation, and the relation between eigenphases δ_i and eigenvalues M_i of the $\boldsymbol{M}$ matrix is equivalent to equations (1) and (7),

$$\tan\delta_i = -(M_i c + d)/(M_i a + b). \tag{8}$$

The described method is very efficient for studying the energy dependence of eigenphases at very low energies in the resonance region and toward zero energy. In particular, we are able to compute eigenphases in the energy region down to 10^{-6} eV. In this region the eigenphases are well described by the two terms of the MERT of O'Malley *et al* [3],

$$\tan\delta = -kS_L - \frac{\pi}{3}\alpha k^2 \tag{9}$$

where the scattering length S_L is given by [2]

$$S_L = \beta\alpha^{1/2}. \tag{10}$$

In order to compute the ^{3}S^e and ^{1}S^e scattering lengths for e$^-$ + Rb, Cs, and Fr collisions, we extrapolate toward zero energy the eigenphases provided by our Dirac R-matrix calculations, by using the relativistic MERT. For $k \to 0$, the s-wave scattering length is defined as $-(\tan\delta)/k$ [13]. Our confidence in the Dirac R-matrix eigenphases for low-energy electron scattering by heavy alkali-metal atoms is based on the excellent agreement with experimental data for the lowest ^{3}P^o resonances of Rb$^-$ and Cs$^-$ [7].

Although MERT contains only two adjusted parameters for each symmetry, it reproduces the energy dependence of the eigenphases in a wide energy range. For the present MERT calculations, the two fit parameters are the Dirac R-matrix eigenphases for two reference energy points between 100 and 200 meV. At 200 meV, the de Broglie wavelength $\lambda = 2\pi(2E)^{-1/2} = 51.82$ of the scattered electron is much larger than the radius of the *short-range* interaction, which may be approximated by the effective atomic radius R_c. In [7], we have estimated R_c as 4.7 for Rb, 5.1 for Cs, and 5.4 for Fr. The most important parameter responsible for the fast variation of the eigenphases in our MERT calculations is the polarizability of the target.

We first discuss results for slow electron scattering by Fr targets and analyse the three J^π symmetries in which we find the terms of the lowest ^{3}P^o resonance of Fr$^-$, as a test case. At low collision energies only a few channels are open. The $J^\pi = 0^-$ case has just one open channel associated with $7sn'p_{1/2}$ configurations ($n' \geqslant 7$), and equation (8) can be applied directly. Here and throughout this letter n' denotes bound and continuum orbitals. The $J^\pi = 2^-$ symmetry is dominated by p-wave scattering. The analysis of the contribution of different channels to

Table 1. MERT parameters η and β for slow e^- + Fr collisions and J^π symmetries that contribute to the $Fr^-(^3P^o)$ resonance. The energies of the $^3P^o_J$ terms from the present relativistic MERT calculations are compared with explicit Dirac R-matrix results in [7].

				$E(^3P^o_J)$ (meV)	
J^π	j	η (eV^{-1})	β	MERT	Reference [7]
0^-	1/2	0.073 79	−0.066 82	12.4	13.2
1^-	1/2	0.104 4	−0.142 9	23.5	24.0
	3/2	−0.814 3	−0.145 0		
2^-	3/2	0.174 6	−0.330 8	40.7	40.8

Table 2. Relativistic MERT parameters η and β for s-wave scattering in e^- + Rb, Cs, and Fr collisions.

	Rb		Cs		Fr	
J^π	η	β	η	β	η	β
0^+	−0.049 38	0.035 12	−0.1762	−0.0662	−0.023 74	0.074 98
1^+	−0.255 8	−0.900 3	−0.5120	−1.0810	−0.378 6	−0.752 5

the eigenvectors of the total Hamiltonian inside an R-matrix sphere of radius 40 shows that p-wave scattering contributes about 97% to the partial cross section for electron scattering in the 2^- symmetry. In this case we can use the ERT model of O'Malley *et al* [3] for higher partial wave contributions, such that the eigenphase sum is

$$\delta_{\rm sum} = -\arctan\frac{M_i c + d}{M_i a + b} + \arctan\frac{\pi\alpha k^2}{(2l_h - 1)(2l_h + 1)(2l_h + 3)} \tag{11}$$

where $l_h = 3$. In equation (11), M_i is the eigenvalue of the M matrix for the dominant channel. For the 1^- symmetry the situation is different, since two p-wave scattering channels dominate, $7sn'p_{1/2}$ and $7sn'p_{3/2}$, and we have to use equation (8) separately for each eigenphase. The same situation was observed for the $^3P^o$ resonances of Rb^- and Cs^- ions.

In table 1 we list the parameters β and η obtained for the four eigenphases discussed above for e^- + Fr collisions. In the $J^\pi = 1^-$ (and $j = 3/2$) symmetry we use the effective range expansion of M, while for the other symmetries we expand M^{-1}. The present *relativistic* MERT calculations for e^- + Fr collisions allow us to resolve the fine structure components of the $^3P^o$ resonance. The $^3P^o_J$ terms in table 1 are compared with earlier Dirac R-matrix calculations [7]. The agreement between the two calculations gives us confidence in the present relativistic MERT method. In our MERT calculations we use the same atomic polarizability for Fr(7s) (317.8) [14] as in [7].

The MERT method is designed to accurately describe the scattering of slow electrons with large de Broglie wavelengths, and thus allows the computation of reliable s-wave scattering lengths. For the calculation of the $^1S^e$ and $^3S^e$ scattering lengths, we have to use the eigenphases in the 0^+ and 1^+ symmetries. The $J^\pi = 0^+$ symmetry has only one (s-wave) channel. In the 1^+ symmetry, the s-wave contributes with 99% to electron scattering for all three targets. In order to compute the eigenphase sum in the 1^+ symmetry, we use equation (11) with $l_h = 2$. Table 2 gives the parameters β and η in the 0^+ and 1^+ symmetries for the three targets. For both symmetries, we use the effective range expansion of M.

The eigenphases, extrapolated to zero energy within the relativistic MERT method, are almost identical with the eigenphases obtained from explicit Dirac R-matrix calculations, except for ultralow energies. The differences between the two sets of eigenphases are negligible

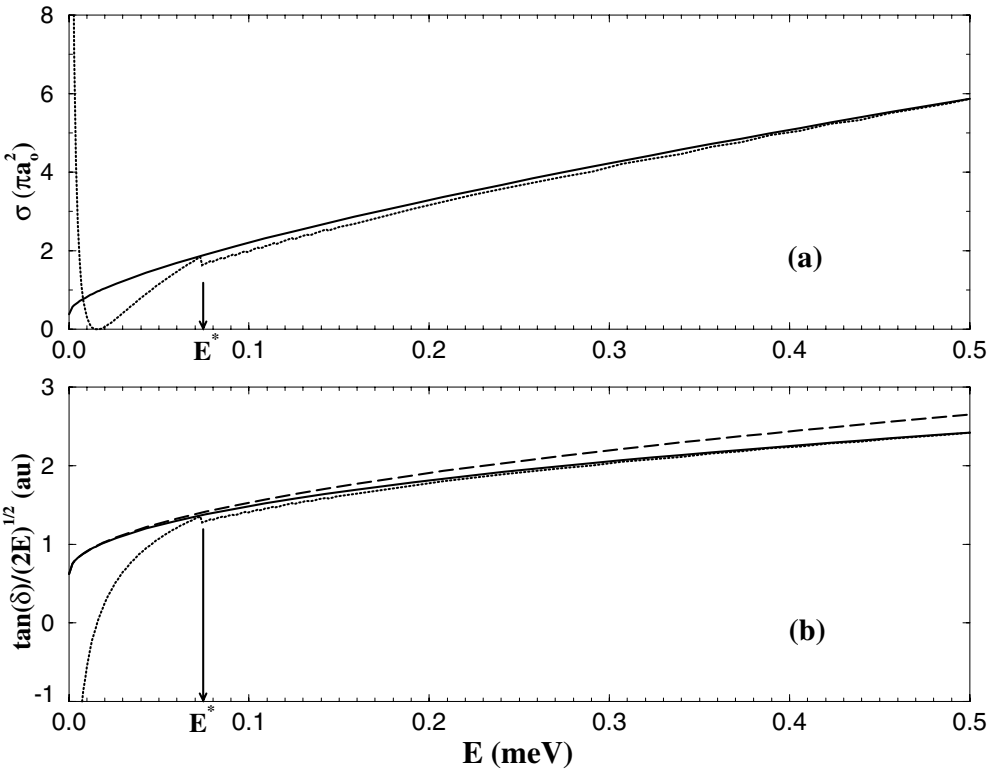

Figure 1. Electron scattering by Rb targets in the $J^\pi = 0^+$ symmetry. Comparison between explicit Dirac R-matrix calculations (dotted curve) and the relativistic MERT extrapolation (full curve) to $E = 0$. (a) Statistically-weighted elastic cross sections and (b) convergence test for the scaled eigenphase δ (according to equation (9), broken curve) for $S_L = 0.627$ (cf table 3). E^* (indicated by an arrow) represents the lower limit of validity for our Dirac R-matrix computations.

above 1 meV. This is demonstrated by the good agreement for the $^3P^o_J$ terms of Fr^-. Below 1 meV, the Dirac R-matrix eigenphase slowly starts to deviate from the MERT extrapolation, reaching a relative difference of 0.9% at 0.3 meV. This difference increases with decreasing E. As an example, we show in figure 1 results below 0.5 meV for e^- + Rb collisions, in the 0^+ symmetry. At 0.074 meV, the Dirac R-matrix eigenphase shows a discontinuity and then drops rapidly to zero at 0.015 meV, which is reflected by a minimum in the Dirac R-matrix cross section (figure 1(a)). Figure 1(b) shows a convergence test for the $^1S^e$ scattering length for e^- + Rb collisions. The broken curve shows $-(\tan\delta)(2E)^{-1/2}$ according to equation (9) for $S_L = 0.627$ (table 3). Our MERT data (full curve) converge to this curve below 0.03 meV.

The unphysical Dirac R-matrix results at energies below 0.1 meV are due to numerical errors in the backward integration in the outer region [9]. Norcross [15] has shown that in the presence of closed channels the wavefunction in the open channel contains errors which accumulate as $A\exp(-\kappa r)$ (κ is the wavenumber in the closed channel and A is a constant) during backwards integration from large distances r of the asymptotic close-coupling equations. Since the scattering length is defined at zero energy, backward integration from extremely large distances would be necessary. But even if we started the backward integration at infinity, we would not be able to provide accurate Dirac R-matrix eigenphases because of the above mentioned arguments. Therefore an alternative procedure to extrapolate eigenphases

Table 3. $^1S^e$ and $^3S^e$ scattering lengths for e^- + Rb, Cs, and Fr collisions compared with previous non-relativistic MERT data [2] and Dirac *R*-matrix results for $^3S^e$ scattering lengths in [7]. Values of the polarizations α for Rb(5s) [16], Cs(6s) [16], and Fr(7s) [14].

	$^1S^e$		$^3S^e$			
Target	This work	Reference [2]	This work	Reference [2]	Reference [7]	α
Rb	0.627	2.03	−16.1	−16.9	−13	319.2
Cs	−1.33	−2.40	−21.7	−22.7	−17	402.2
Fr	1.34	—	−13.4	—	−12	317.8

down to $E = 0$ is necessary.

The $^1S^e$ and $^3S^e$ scattering lengths derived from our relativistic MERT calculations for electron scattering by Rb, Cs, and Fr atoms are given in table 3. We have checked the accuracy of the MERT results by choosing different energy reference points and looking at the corresponding variations of the scattering length. The resulting uncertainty can be estimated as $\pm 1\%$. For all targets our new results for the $^3S^e$ scattering lengths based on equation (9) for $k \to 0$ are larger (in absolute magnitude) than the previous estimations [7] based solely on the Dirac *R*-matrix calculations. The Dirac *R*-matrix calculations in [7] were a qualitative estimate for the sign of the $^3S^e$ scattering lengths for e^- + Rb, Cs, and Fr collisions. These calculations do not provide accurate values. Higher orders of k should have been included in equation (9) in order to provide accurate values for the $^3S^e$ scattering lengths in [7].

Table 3 compares our relativistic MERT results with previous non-relativistic calculations for e^- + Rb and Cs collisions from [2] and shows the atomic polarizabilities used in the present calculations for Rb(5s) [16], Cs(6s) [16], and Fr(7s) [14]. The large values of α explain the good agreement between the $^3S^e$ scattering length data from the two independent calculations. Indeed, the spatial wavefunction of the $^3S^e$ state is antisymmetric and, therefore, the long-range effective interaction (which is dominated by the polarization interaction) is more important than for $^1S^e$ scattering. Since the polarizabilities used in the present calculations are not significantly different from those used in [2] (319.2 instead of 328 in [2] for Rb(5s), and 402.2 instead of 402 in [2] for Cs(6s)), little change was found in the $^3S^e$ scattering length values. The large negative $^3S^e$ scattering length indicates that the attractive polarization potential supports a $^3S^e$ virtual state rather than a bound state.

The $^1S^e$ scattering state has a symmetric spatial wavefunction and short-range electronic correlations are more important than for the $^3S^e$ case. With respect to the previous non-relativistic two-channel calculations [2], the present Dirac *R*-matrix calculations use a much larger basis set (for details see [7]) and thus better represent the short-range correlation effects. This explains the significant difference between our present $^1S^e$ scattering lengths and the results of [2].

In summary, we have provided new, accurate values of the $^1S^e$ and $^3S^e$ scattering lengths for electron scattering by Rb, Cs, and Fr atoms. Our calculations were performed within the relativistic MERT method and used two fit parameters that we adjusted to eigenphases computed within the Dirac *R*-matrix method for collision energies between 100 and 200 meV.

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