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Negative-ion resonances in total cross sections for slow electron-sodium collisions

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The interaction of electrons and atomic sodium was studied by using the momentum space coupled-channel optical method at low-impact energies. Total scattering cross sections have been calculated, and negative-ion resonances have been located. The present calculation results are in good agreement with available experimental data and previous theoretical results. We have obtained resonance features at 4.166 and 4.502 eV and also found possible resonance structures near the ionization threshold in the total cross sections.

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I. INTRODUCTION

In the past few decades, the alkali metal atoms have been the focal subjects for studies of low-energy electron-atom interactions, including scattering and binding to form negative ions and resonances [1–5]. Negative-ion formation in electron-sodium (*e*-Na) scattering has attracted substantial theoretical and experimental efforts owing to its extreme sensitivity to the electron correlation effects. Experimental studies for sodium negative-ion resonances have been carried out in electron scattering [6–12], laser photodetachment technology [13], and electron transmission spectroscopy [14,15]. On the theoretical side, the low-lying negative-ion states were predicted by several different theoretical models, such as the close-coupling approach [16–18], the multiconfigurational Hartree-Fock method [19], and variational [20], effective-range [21], and relativistic R-matrix techniques [22]. A comprehensive review can be found in the article of Buckman and Clark [23]. Although *e*-Na scattering and the low-lying spectra of Na negative ions have been extensively studied, most of previous theoretical studies and experimental observations of the *e*-Na resonances have concentrated on just the lower features. Relatively few autodetaching features have been observed or calculated near the excitation thresholds, and little is known about the higher lying resonances within a few electron volts of the ionization limit of the Na atom. The insufficient experimental and theoretical data on the spectra of Na negative ions in this energy region motivates this work. In this article, we present results for the negative-ion resonance in *e*-Na scattering below the threshold of ionization. These results not only support the previous observations of Johnston and Burrow [15] but also demonstrate possible additional resonances.

The present results are obtained by investigating the energy dependence in electron-sodium scattering using the momentum space coupled-channel optical (CCO) [24] method. The formation of temporary negative ion is caused by the interaction of extra electrons with target atoms. The temporary capture of the incident electron in the potential formed by a combination of the long-range polarization potential and the short-range potential of the target induces a sensitive variation in the scattering cross sections, which indicates the presence of a resonance state of the projectile electron-atom system [23]. The CCO method has been applied for more than two decades in studies of electron collisions with atoms [24–26]. A distinct feature of the model is that it can represent many-body interactions in a convenient way by using an *ab initio* complex equivalent local potential. The real part of the potential represents the polarization of target. The method allows us to take the long-range polarization and short-range interaction of the incident electron and target accounted for in the calculation. The method has been used to investigate the energy-dependent phenomena in electron-hydrogen scattering, and good agreement with experiments has been obtained [27]. The detailed description of the CCO method has been given in [24], and here we briefly review the essential features.

II. THEORETICAL DETAILS

It is essential to note that the space of target states has been split into two parts: P and Q. In the present calculation, eight discrete channels ($3, 4, 5s$; $3, 4, 5p$; $3, 4d$) are explicitly coupled in P space for sufficient convergence and continuum and are included in Q space. The total cross section is calculated by solving the CCO equations [24] in momentum space:

$$\langle \mathbf{k} i | T_S | 0 \mathbf{k_0} \rangle = \langle \mathbf{k} i | V_S^{(Q)} | 0 \mathbf{k_0} \rangle + \sum_{j \in P} \int d^3 q \frac{\langle \mathbf{k} i | V_S^{(Q)} | j \mathbf{q} \rangle \langle \mathbf{q} j | T_S | 0 \mathbf{k_0} \rangle}{E^{(+)} - \varepsilon_j - q^2/2}, \quad (1)$$

where i, j represent target states in P space and Q projects the continuum and the remaining discrete states. The subscript S indicates the total spin. $V_S^{(Q)}$ has two parts, the electron-target potential V_S and the complex, nonlocal polarization potential $W_S^{(Q)}$:

$$V_S^{(Q)} = V_S + W_S^{(Q)}. \quad (2)$$

The real part of optical potential are used in the coupled channels since the impact energy is less than the ionization threshold of Na. The real part describes virtual (off-shell) excitation of the Q space. At long range, the potential has asymptotic behavior of the dipole polarization potential $-[\alpha/(2r^4)]$, where α is the dipole polarizability of the target.

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The form for the matrix element of the polarization potential is

$$\langle \mathbf{k}'i|W_S^{(Q)}|j\mathbf{k}\rangle = \sum_{n\in Q}\langle \mathbf{k}'i|V_S|\Psi_n^{(-)}\rangle \frac{1}{E^{(+)}-E_n}\langle \Psi_n^{(-)}|V_S|j\mathbf{k}\rangle, \tag{3}$$

where $|\Psi_n^{(-)}\rangle$ represents the time reverse of the exact state vector for a reaction starting in channel n and n is a discrete notation for the three-body continuum state.

The model used here is

$$|\Psi_n^{(-)}\rangle = |c\psi^{(-)}(\mathbf{q}_<)\mathbf{q}_>\rangle, \tag{4}$$

where $\mathbf{q}_>$ and $\mathbf{q}_<$ are the greater and lesser, respectively, of the absolute momenta of the outgoing particles, c is the remaining core, $\langle \mathbf{r}|\psi^{(-)}(\mathbf{q}_<)\rangle$ is a Coulomb wave orthogonalized to the orbital from which the electron is removed, and $\langle \mathbf{r}|\mathbf{q}_>\rangle$ is a plane wave. This approximation accounts for the Coulomb screening effect for the ejected electron.

The direct potential matrix element is calculated by an analytic form. The exchange matrix element has a similar analytic form in the equivalent-local approximation and angular momentum projection approximation made for the whole polarization potential. The polarization potential element is then calculated in the variable K,

$$\langle \mathbf{k}'i|W_S^{(Q)}|j\mathbf{k}\rangle = \sum_{l'',m''} i^{l''} C_{l'l''l}^{m'm''m} U_{l'l''l}(K) Y_{l''m''}(\hat{\mathbf{K}}), \tag{5}$$

where lm and $l'm'$ are the orbital angular momentum quantum numbers of the states i and j, respectively, and

$$\mathbf{K} = \mathbf{k} - \mathbf{k}'. \tag{6}$$

The half-on-shell approximation

$$\tfrac{1}{2}\mathbf{k_j}^2 = E - \varepsilon_j \tag{7}$$

is made for the amplitudes (3), reducing the computation of the polarization potential to the function $U_{l'l''l}(K)$ obtained by inverting Eq. (5):

$$\begin{aligned} &U_{l'l''l}(K) \\ &\quad = \sum_{m'',m'} C_{l''\ l'\ l}^{m''m'm} \int d\hat{\mathbf{K}} \langle \mathbf{k}'i|W_S^{(Q)}|j\mathbf{k}\rangle i^{-l''} Y_{l''m''}^{*}(\hat{\mathbf{K}}). \end{aligned} \tag{8}$$

The present calculation was carried out using the same quadrature points for solving the coupled integral equation (1) over a range of energies, thus making the off-shell potential matrices energy independent. For computation, we make a partial-wave expansion of the T_S and $V_S^{(Q)}$ matrix elements, for total angular momentum quantum number J, by

$$\begin{aligned} &\langle \mathbf{k}'i|T_S|j\mathbf{k}\rangle \\ &\quad = \sum_{L,M,L',M',J,K} \langle \hat{\mathbf{k}}'|L'M'\rangle C_{L'l'J}^{M'm'k} T_{nLl}^{n'L'l'(J)}(k',k) C_{LlJ}^{Mmk} \langle LM|\hat{\mathbf{k}}\rangle, \end{aligned} \tag{9}$$

where

$$\langle \hat{\mathbf{k}}|L'M'\rangle \equiv Y_{LM}(\hat{\mathbf{k}}), \tag{10}$$

C_{LlJ}^{Mmk} is a Clebsch-Gordan coefficient, and $T_{nLl}^{n'L'l'(J)}(k',k)$ is the partial matrix element. The definition of $V_{nLl}^{n'L'l'(J)}$ is analogous to Eq. (9) with $V_S^{(Q)}$ substituted for T_S.

The total cross section is then obtained by summing the partial-wave cross sections:

$$\sigma_{ij} = (2\pi)^4 \frac{k_i}{k_k} \frac{\widehat{S}^2}{\widehat{l}^2} \frac{1}{4\pi} \sum_{L,L',J} (2J+1)\left|T_{nLl}^{n'L'l'(J)}\right|^2. \tag{11}$$

In the present calculation, the target states were represented by frozen-core Hartree-Fock wave functions in Slater-type basis [28], and up to fifty partial waves were included in the sum for the total cross sections. The CCO equation (1) was solved in the whole energy region we investigated for each partial wave T-matrix element. The calculations have been done at intervals of 0.01 eV for incident energies less than 3.0 eV and at intervals of 0.001 eV for energies from 3.0 to 5.2 eV.

III. RESULTS AND DISCUSSION

We have investigated the energy dependence of the total scattering cross sections in *e*-Na scattering, where the character of resonance can be identified. The present total cross sections are displayed in Figs. 1 and 2, along with available experimental data and theoretical results: the absolute total cross-section measurements by Rubin [8] and Kasdan *et al.* [11], the relative measurement of Perel *et al.* [7] that have been normalized to the reported results of Moores and Norcross [18] at 5 eV, the recent absolute total cross sections measured by Kwan *et al.* [29], the close-coupling calculation results of Karule [17] and Moores and Norcross [18], the R-matrix calculation results of Walters [22], and the convergent close-coupling (CCC) calculation results of Bray [30]. Agreements between the present calculation results and experimental measurements, especially with the results of Rubin [8] both in the shape and magnitude, are excellent. It is very interesting to note that

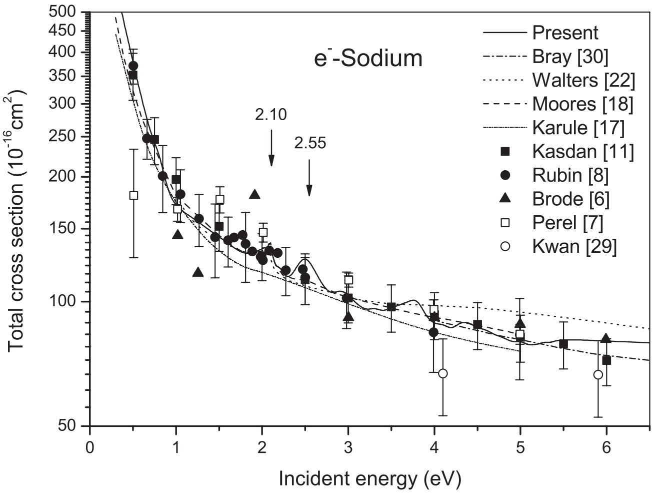

FIG. 1. Present calculation of total cross sections for *e*-Na below the ionization threshold along with available experimental and theoretical results. The calculation intervals were 0.01 eV. The centers of the resonances are marked with arrows.

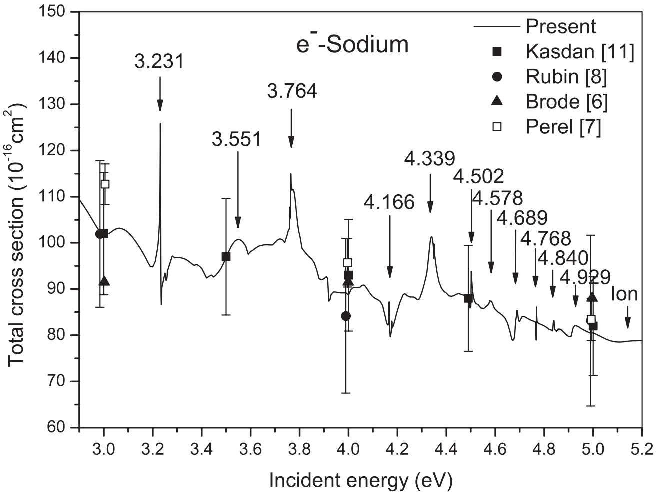

FIG. 2. Detailed calculation of total cross sections for *e*-Na from 3.0 eV to the ionization threshold at intervals of 0.001 eV. The centers of the resonances are marked with arrows.

there are some resonance structures exhibited in the present total scattering cross sections.

The peaks located at 2.10 and 2.55 eV in the calculated cross sections displayed in Fig. 1 are in good agreement with the experimental measurement of Rubin [8], in which the positions of peaks are at 2.08 and 2.47 eV, respectively. The feature at 2.10 eV in the present calculation is due to the overlapping of two resonances which belong to ^1D and ^1P symmetries. However, the four-state ($3s$-$3p$-$4s$-$3d$) close-coupling method of Moores and Nocross [18] obtained these resonances at 2.00 eV. The difference between the present calculation and Moores and Nocross's [18] results is probably caused by the different channels used in the two calculations. The variational calculation of Sinfailam and Nesbet [20] predicted the two resonances at 2.10 eV, which are coincident with present results. Johnston and Burrow [15] observed a structure at 2.0–2.2 eV that contained the overlapping of $3p3p\ ^1D$ and $3p4s\ ^1P^o$ resonances and a Wigner cusp due to the opening of the first inelastic channel. Another experiment of Andrick, Eyb, and Hofmann [10] for the differential elastic scattering also showed the strong influence of the ^1D and ^1P resonances near $3p$ excitation threshold in cross sections. The next peak that we locate at 2.55 eV with ^3F symmetry should correspond to the feature at 2.57 eV with a configuration of $3p3d\ ^3F$ as observed by Johnston and Burrow [15]. The experiment of Rubin [8] also exhibited a relatively small peak at 2.47 eV in the total cross sections. Such ^3F resonance has not been predicted by any other theoretical calculations yet, although several calculations (Burke and Mitchell [31], Moores [32], Scott *et al.* [33]) have predicted a similar ^3F resonance for the heavier alkali metals above the first inelastic threshold.

Detailed results from 3.0 eV up to the ionization threshold are shown in Fig. 2, and several resonance structures were obtained in the total scattering cross sections for *e*-Na in this energy region. We have identified a narrow resonance at 3.231 eV with the symmetry of ^1S, just above the $4s$ excitation threshold, which confirms the experimental observation of Johnston and Burrow [15]. In their transmission spectrum, a quite narrow resonance was observed at 3.20 eV with the electron configuration of $4s4s\ ^1S$. The multiconfigurational Hartree-Fock calculation of Fung and Matese [19] also predicted an ^1S state of Na$^-$ at 3.04 eV, which was much less than the results of the present calculation and measurement of Johnston and Burrow [15]. It is interesting to note that the result predicted by the authors is below the $4s$ threshold (3.193 eV) and that a much smaller number of resonances were obtained near other excitation thresholds in their calculation. It has been suggested by the authors that this is probably caused by the smaller number of single-particle states with large spatial extent that are included in the configuration mixing or the weaker interactions in the *e*-Na system [19]. The next feature in the present cross sections at 3.551 eV with ^1D symmetry can support the structure of $4s3d\ ^1D$ at 3.53 eV in Johnston and Burrow's transmission spectrum data [15]. No other theoretical calculations have been performed yet in this energy region. For higher lying resonances near the $4p$ excitation threshold, we find a prominent feature located at 3.764 eV, just above the $4p$ excitation threshold, which should belong to the symmetry of ^1D with configuration $4p4p$. Johnston and Burrow [15] observed a strong family of ^1D resonance in K$^-$, Rb$^-$, and Cs$^-$ with the configurations of $5p5p$, $6p6p$, and $7p7p$ respectively. No corresponding $4p4p$ resonance was observed for Na$^-$. However, a possible assignment of this family resonance in Na$^-$ could be made in 3.8–3.9 eV from the extrapolation of the analogous features in the heavier alkali metals [15,34]. The absence of such a feature in Na$^-$ needs further experimental consideration.

Above $4p$ excitation threshold, several possible resonance features appear at 4.166, 4.339, 4.502, 4.578, 4.689, 4.768, 4.804, and 4.929 eV in the present total cross sections. Note that there are two resonance features at 4.11 and 4.49 eV that have been observed by Johnston and Burrow [15]. To the best of our knowledge, no further experimental or theoretical results are available in the literature for the higher lying resonances reported in this work. The ^3D resonance at 4.166 eV and a narrow resonance at 4.502 eV obtained by the present calculation could support the two observed features of $5s4d\ ^3D$ at 4.11 eV and the other one at 4.49 eV in the experiments of Johnston and Burrow [15]. Additionally, in

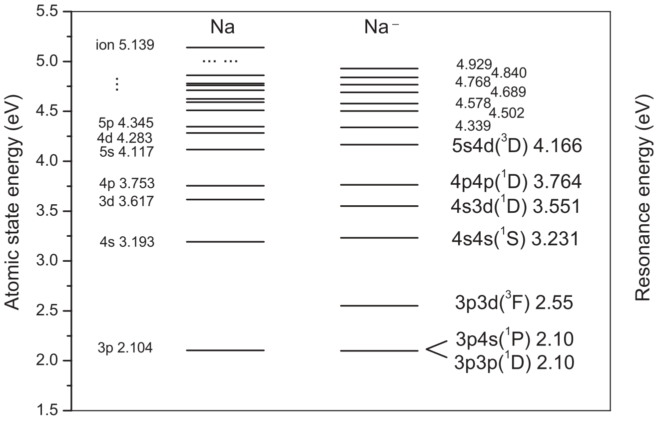

FIG. 3. Approximate energy level diagram of Na$^-$ and Na bound states. The energies were referenced to the ground state of the Na atom.

TABLE I. Configurations and energies for resonances in *e*-Na below ionization threshold. The energies were referenced to the ground state of the Na atom. The resonance energies of Johnston and Burrow [15] in brackets were obtained from the extrapolation of the family resemblance among the resonances of the heavier alkali metals. Additionally, an uncertainty of ±0.03 eV was introduced by the authors to all the features in their experiment.

		Experimental results	**Theoretical results**		
Configuration	Present	Johnston and Burrow [15]	Moores and Norcross [18]	Fung and Matese [19]	Sinfailam and Nesbet [20]
$3p3p\ ^1D$	2.10	2.10	2.00		2.10
$3p4s\ ^1P$	2.10	2.10	2.00		2.10
$3p3d\ ^3F$	2.55	2.57			
$4s4s\ ^1S$	3.231	3.20		3.04	
$4s3d\ ^1D$	3.551	3.53			
$4p4p\ ^1D$	3.764	(3.8–3.9)			
$5s4d\ ^3D$	4.166	4.11			
–	4.339	(4.3–4.4)			
–	4.502	4.49			
–	4.578	(4.59)			
–	4.689				
–	4.768				
–	4.840				
–	4.929				

their experiments, another two family resonances obtained by the extrapolation method as mentioned previously, should be located at 4.3–4.4 eV and 4.59 eV, respectively, which probably correspond to the possible resonances at 4.339 and 4.578 eV predicted in the present calculation. Near the extreme ionization limit, the absence of the measurement of Johnston and Burrow [15] for Na^- above 4.70 eV is probably due to the restriction of the experimental condition. However, the large successive resonance series up to the ionization threshold were observed clearly in the heavier alkali metals, and some still higher features could be grouped into families [15]. It is hoped that our results will provide useful information for further theoretical and experimental studies.

Figure 3 shows the approximate energy level diagram of Na^- analogous with the bound states of Na. In Table I, we compare our calculated results with previous theoretical results and available experimental observations. The application of the CCO method to the energy-dependent phenomena and electron-sodium resonances gives good agreement with experiments and other calculations. The present results not only confirm experimental observations but also suggest additional resonances. The higher lying resonances that we have obtained near the ionization threshold still need further experimental confirmation.

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