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Static and dynamic polarizabilities of Na$^-$ within a variationally stable coupled-channel hyperspherical method

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Using a model potential representation combined with a variationally stable method, we present a precise calculation of the electric dipole polarizabilities of the sodium negative ion (Na$^-$). The effective two-electron eigensolutions for Na$^-$ are obtained from a hyperspherical coupled-channel calculation. This approach allows efficient error control and insight into the system's properties through one-dimensional potential curves. Our result of 1018.3 a.u. for the static dipole polarizability is in agreement with previous calculations and supports our results for the dynamic polarizability, which has scarcely been investigated hitherto.

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Negative ions have been commonly used as a ground test for theoretical and numerical approaches owing to the great importance of the electronic correlation in a short-range potential. Such studies have been founded on the advances of experimental techniques, allied to the interest in fields ranging from atmosphere studies [1,2] to astrophysics [3–5]. The alkali-metal negative ions can be related to the hydrogen negative ion concerning the optically active two-electron correlation characteristic of the spectral lines. Only few weakly bound states have been observed for such systems. Indeed, the best known species possess a single bound state.

Owing to the large number of physical and chemical properties related to polarizabilities, there exists an extensive interest in their accurate calculation. For instance, the dynamic or frequency-dependent polarizability is closely related to the van der Waals dispersion coefficients in the long-range interactions of atomic and molecular species. A comprehensive review of electric dipole polarizabilities was given by Bonin and Kadar-Kallen [6], in which both theoretical methods and experimental techniques were examined.

The present work investigates the static as well as the dynamic electric dipole polarizability of the sodium negative ion (Na$^-$). Results for the static dipole polarizability from different methods are found in the literature [7–13]. Contrary to the polarizability of the lithium negative ion (Li$^-$), on which available data in the literature have been focused [14–20], the values for the frequency-dependent polarizability of Na$^-$ have only been estimated from formulas derived by Lamm *et al.* [10] and Delone *et al.* [11]. Lamm *et al.* [10] used an asymptotic form for the wave function and a one-parameter pseudopotential. Delone *et al.* [11] employed a quasiclassical description with a one-particle short-range potential for the alkali-metal negative ion as well as the asymptotic character of the wave function to achieve the behavior of the frequency dependence. Both were analytically derived results and in fact, to our knowledge, there does not exist any other result in the literature for the dynamic polarizability of the sodium anion. The scarceness of results from other authors evidences the difficulties involved in this kind of calculation. One of the reasons is the very small electron affinity of the neutral sodium, requiring accurate and stable methods in the achievement of wave functions. The lack of experimental data on the polarizabilities of Na$^-$ motivates this work, since accurate theoretical results can aid in developing further experiments.

As an alternative to the all-electron description of the system, the interactions of the valence electrons with both the nucleus and the electronic closed shells are described through a model potential [21]. This approach has been successfully employed for alkali-metal atoms and anions due to a rather compact core that has little effect on the outer valence electrons, especially the more diffuse, larger orbitals of a negative ion. The core polarizability owing to the one- and two-electron fields, also taken into account, improves the calculations, leading to a very precise electron affinity [22].

In order to provide precise results, Gao and Starace's second-order variationally stable approach is employed in this work [23], avoiding the explicit summation over intermediate states and allowing the determination of polarizabilities using only the ground-state wave function. This is an important aspect, considering the efforts demanded by the second-order perturbation calculations, which require the full description of the complete bound and continuum states of the sodium ion. Within this variational approach, a basis formed by Slater orbitals provides fast convergent results, as shown for the one- and two-electron systems studied so far [23–25]. Moreover, applications to larger atomic systems using the Hartree-Fock description for the target can also be found [24,26]. Additionally, a molecular system (H_2) was treated employing the variationally stable method, with good results [27].

For the wave function calculation, the hyperspherical adiabatic approach (HAA) is applied [28]. This is an efficient method to study strongly correlated few-body systems for both theoretical and numerical aspects. The HAA provides a one-dimensional potential curve description of the energy levels, with precise results, using few coupled radial channels. For the potential model of the sodium ion, the HAA is especially suited due to the upper and lower energy bounds obtained from simple uncoupled approaches [29,30], both using only the lowest potential curve, with and without the diagonal nonadiabatic radial coupling, respectively. Such behavior has also been observed for the sodium anion model-potential approach [22].

The model potential used in this study to represent each valence electron interaction with the positive ionic core is defined as (atomic units are used throughout the paper)

$$V(r) = -\frac{1}{r}[Z_c + (Z - Z_c)e^{-a_1 r} + a_2 r e^{-a_3 r}] - \frac{\alpha_c}{2r^4}[W_3(r/r_c)]^2, \tag{1}$$

where $Z=11$ is the nuclear charge, $Z_c=1$ is the core's charge, and $\alpha_c=0.9457$ a.u. is the Na^+ polarizability [31]. The remaining empirical parameters are obtained by a fitting procedure in order to reproduce the experimental binding energies [32] of the neutral system. For the sodium atom, the set of parameters used is the one calculated in Liu and Starace's paper [33]. The last term in Eq. (1) is a long-range nonlocal contribution due to the core polarization. The cutoff function $W_n(r)$ (cf. Ref. [22]) represents the reduction of electron polarization effects over the core as the electrons approach the nucleus. The core polarization due to the two-electron effects is considered through the dielectronic polarization potential

$$V_{12}(\mathbf{r}_1,\mathbf{r}_2) = -\frac{\alpha_c}{r_1^2 r_2^2}\cos\theta_{12} W_3(r_1/r_c)W_3(r_2/r_c). \tag{2}$$

For the sodium anion in the two-electron picture, hyperspherical coordinates are introduced, correlating the two electron spherical radial variables r_1 and r_2 by means of a Cartesian-polar-like transformation, i.e., $R=(r_1^2+r_2^2)^{1/2}$ and $\alpha=\tan^{-1}(r_1/r_2)$. The spherical angular coordinates $\{\theta_i,\phi_i\}$ of the electrons are not changed. An important practical aspect of the adiabatic approach is the convergence monitoring of the energy calculations by controlling the number N_c of coupled radial channels considered in the adiabatic expansions [22]. For genuine two-electron systems, such as H^- and the isoelectronic series of helium, the uncoupled radial equation ($N_c=1$) is usually sufficient to furnish the bound states, even for the loosely bound negative ion.

The perturbative matrix element for a second-order transition between an initial state $|i\rangle$ and a final state $|f\rangle$ is written as

$$T^{(2)}_{i\to f}(\omega) = \langle f|D\frac{1}{E_i+\omega-\hat{H}}D|i\rangle, \tag{3}$$

where $D=\boldsymbol{\epsilon}\cdot(\mathbf{r}_1+\mathbf{r}_2)$ is the electric dipole operator in the length form, $\boldsymbol{\epsilon}$ is the light polarization vector, E_i is the energy of the initial state, ω is the photon frequency, and $\hat{H}$ is the unperturbed Hamiltonian. Using the variationally stable method of Gao and Starace [23–25], the transition matrix element [Eq. (3)] can be cast in the form

$$T^{(2)}_{i\to f}(\omega) = \langle f|D|\lambda\rangle + \langle\lambda'|D|i\rangle - \langle\lambda'|E_i+\omega-\hat{H}|\lambda\rangle, \tag{4}$$

where $|\lambda\rangle$ and $\langle\lambda'|$ are unknown intermediate functions related to $|i\rangle$ and $\langle f|$ by one-photon transitions, respectively. The transition rate in Eq. (4) is variationally stable to second order with respect to any deviations of the intermediate functions from their exact values [23]. In other words, the first-order corrections cancel out mutually in this unique combination of the three matrix elements. For the two-electron problem, the Hamiltonian in hyperspherical coordinates is used due to the suitability of this representation. In addition, the initial- and final-state wave functions as well as the intermediate functions are adiabatically expanded in the hyperspherical form. In order to evaluate the integrals, the unknown functions are expanded in Slater orbitals comprising a free parameter β_μ, whose determination is further described. The coefficients of the expansions are attained imposing the variational principle [23–25]. In terms of the second-order transition matrix element, the frequency-dependent polarizability is calculated by replacing the final-state wave function $\langle f|$ by the initial-state wave function $\langle i|$ as follows:

$$\alpha(\omega) = -[T^{(2)}_{i\to i}(+\omega) + T^{(2)}_{i\to i}(-\omega)]. \tag{5}$$

In the static limit, i.e., the photon frequency $\omega\to 0$, the expression for the polarizability is reduced to $\alpha(0) = -2T^{(2)}_{i\to i}(0)$.

Preceding our results for the static and dynamic dipole polarizability of the Na^- ground state, some general computational aspects are briefly discussed. All calculations have been accomplished in the length gauge. In each numerical calculation, REAL*16 (quadruple) precision is used in our codes to minimize numerical error propagation and to deal accurately with a mix of small and large numbers. The hyperspherical potential curves $U_\mu(R)$ have been obtained as briefly described above and presented in detail in Ref. [22]. In order to achieve the static and dynamic dipole polarizabilities, potential curves as well as nonadiabatic couplings for both ${}^1S^e$ and ${}^1P^o$ states are required by the selection rules. In this paper, the calculations of Ref. [22] have been extended to ${}^1P^o$ states. The number of coupled hyperspherical angular channels is related to the maximum value of the electronic angular momenta $l_1^{\max}=l_2^{\max}=l_{\max}$ of each optically active electron, set to provide the desired convergence for the potential curves and nonadiabatic couplings for all values of R. For the individual angular momenta, the maximum value $l_{\max}=4$ has been used for both ${}^1S^e$ and ${}^1P^o$ states, whose corresponding potential curves are shown in Fig. 1. In the calculation of the hyperradial functions, $N_c=3$ coupled equations [22] have been used. This set of parameters provides an electron affinity of 0.020 117 a.u. (547.407 meV) for the sodium atom [22], which compares very well with the experimental value of 0.020 136 a.u. (547.926 meV) [34]. Figure 1 shows the corresponding ground-state energy (−0.417 949 Ry) as a horizontal dashed-line segment in the lowest potential curve. An indication of the hyperspherical method efficiency is the precision of the quasiseparable ap-

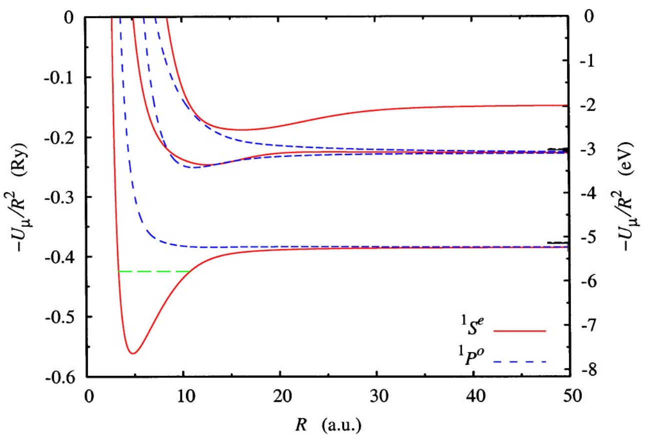

FIG. 1. (Color online) Hyperspherical $^1S^e$ and $^1P^o$ potential curves for Na^- states. The horizontal dashed-line segment represents the bound-state energy (in rydbergs).

proximation (one radial channel), which led to a Na^- bound state result with relative error to the experimental value of only 0.51%. A further inclusion of $N_c = 3$ coupled channels drops the error to only 0.009%.

The choice of parameter β_μ is arbitrary and, for consistency reasons, the ground-state energy E_i used in Eq. (4) is the corresponding hyperspherical value for the number of channels included in our calculations. In order to reduce numerical error in the $N_c = 3$ calculation, the value of $\beta_\mu = 0.71$ was chosen by an error minimization procedure for 13 terms in the expansions. As a result, the three matrix elements of Eq. (4) are identical within 24 digits of accuracy, showing an excellent convergence. Additionally, the ability of the coupled-channel hyperspherical method to provide not only accurate and precise electron affinities (for Na, the relative error to the experimental value is 0.09% [22]) but also good quality wave functions [25,35] has been shown. Indeed, Masili and Starace [25(b)] stressed that the variationally stable method combined with the HAA furnishes results for polarizabilities that possess almost the same level of accuracy as for the ground-state energy.

Table I presents a comparison of our best value for the static polarizability with available theoretical results of other authors. Two of the listed results are rather too low [11] or too high [7], although Langhoff and Hurst [7] highlighted that their polarizability value is unreliable due to the difficulties in constructing the Hartree-Fock wave functions. Our static polarizability result compares best with the value of Moccia and Spizzo [12] using a diagonalization method in an L^2 basis.

TABLE I. Comparison of our present best calculation for the static electric dipole polarizability of Na^- with theoretical results of other authors.

Present result	1018.3
N.C. Pyper *et al.* (1993) (Ref. [13])	1090.2
R. Moccia and P. Spizzo (1991) (Ref. [12])	1032.7
N.B. Delone *et al.* (1986) (Ref. [11])	381.1
G. Lamm *et al.* (1978) (Ref. [10])	1089.7
D.L. Moores and D.W. Norcross[a] (1974) (Ref. [9])	989.9
D.L. Moores and D.W. Norcross[b] (1974) (Ref. [9])	1058.9
R.F. Stewart *et al.* (1974) (Ref. [8])	1069
P.W. Langhoff and R.P. Hurst (1965) (Ref. [7])	1982

[a] Length gauge result.

[b] Velocity gauge result.

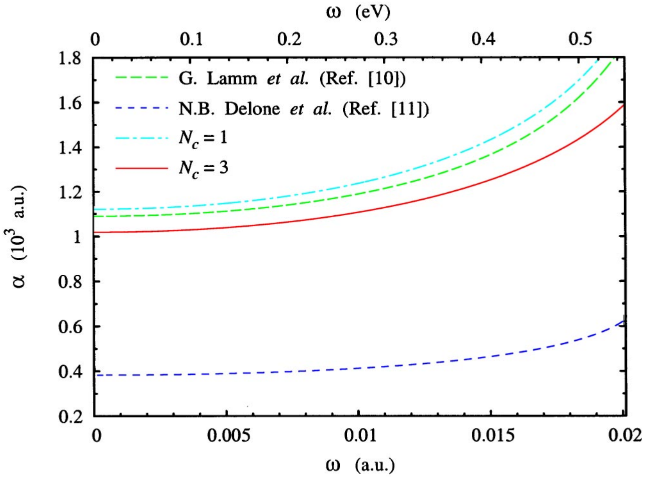

FIG. 2. (Color online) Comparison of the dynamic polarizability with results from the literature.

Varying the photon frequency ω in the transition matrix [Eq. (4)], one obtains the dynamic polarizability. In Fig. 2, our uncoupled result $(N_c = 1)$ and the calculation using the three most important channels $(N_c = 3)$ are compared with estimates from asymptotic calculations of Lamm *et al.* [10]. One notes that the simple uncoupled calculation is comparable to the result of Lamm *et al.* [10], evidencing the quality of the combined methods. As far as we are aware, there exists only one other result for the dynamic polarizability, by Delone *et al.* [11], but their quasiclassical treatment using a one-particle model potential neglects the crucial correlation interaction between the two outermost electrons, and consequently does not lead to precise results for the polarizability. Indeed, as shown in Table I, their static polarizability value is 2.60-2.86 times smaller than the others listed. However, the behavior of the dynamic polarizability is similar to the results of Lamm *et al.* [10] and to our present calculation, especially for small values of the photon frequency, as seen in Fig. 2. A further inclusion of additional channels in our calculation plays a minor role in the convergence. In fact, this small contribution to both energies and polarizabilities has also been observed for H^- [25(a)].

In summary, a calculation of the static and frequency-dependent dipole polarizability of the sodium negative ion (Na^-) has been presented. This paper adds results to the scarcely investigated dynamic polarizability of the sodium anion. The variational procedure employed is a practical approach to be applied as an alternative to the direct perturbation calculation, which requires the knowledge of the wave function of all unperturbed bound and continuum states of the sodium negative ion. The variational approach requires only the ground-state solution and yet provides fast-convergent and precise results. The Gao and Starace's variationally stable method combined with the coupled-channel hyperspherical description of the wave function of the effective two-electron Na^- has proved to be capable of providing very precise and accurate results for the second-order perturbative process. Those are compelling results and strongly suggest the calculation of two-photon detachment cross sections of Na^-. Likewise, this methodology can be extended to other alkali-metal negative ions of interest.

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