PHYSICAL REVIEW A **81**, 064505 (2010)

Binding energy and structure of e^{+}Na

J. Shertzer[1] and S. J. Ward[2]
[1] *Department of Physics, College of the Holy Cross, Worcester, Massachusetts 01610, USA*
[2] *Department of Physics, University of North Texas, Denton, Texas 76203, USA*

(Received 30 March 2010; published 28 June 2010)

We calculate the nonadiabatic binding energy and geometry of the weakly bound state of e^{+}Na. We use the Peach model potential, which includes both the dipole and an effective quadrupole term in the polarization, to describe the interaction of the electron and positron with the ion core. The effective three-body Schrödinger equation is solved with the finite element method. Because the model potential gives rise to three spurious states, the true ground state of e^{+}Na is embedded in a dense spectrum of spurious states. We develop a method for extracting the correct ground state for e^{+}Na, even when the energy is nearly degenerate with a spurious level. The calculated value for the binding energy is consistent with other calculations.

DOI: 10.1103/PhysRevA.81.064505 PACS number(s): 36.10.Dr, 31.15.−p

Introduction. Hydrogen cannot bind a positron. The total energy of e^{+}H is less than the energy of the hydrogen atom, but not less than the energy of positronium. The system dissociates into a proton and a positronium atom. Both lithium and sodium can bind a positron because the static dipole polarizability of these atoms is significantly larger than that of hydrogen. For the positronic alkali-metal ion e^{+}A, where $E_{\mathrm{Ps}} < E_{\mathrm{A}}$, the binding energy is computed with respect to the dissociation channel: $\varepsilon = E_{\mathrm{Ps}} + E_{\mathrm{A}^{+}} - E_{e^{+}\mathrm{A}}$. If one uses a model potential to describe the interaction of the valence electron and positron with the ionic core, neither E_{A} nor $E_{e^{+}\mathrm{A}}$ includes the energy of the ionic core; in that case, the binding energy of the positronic ion is given by $\varepsilon = E_{\mathrm{Ps}} - E_{e^{+}\mathrm{A}}$.

Model potentials for atomic sodium attempt to replicate the interaction between the valence electron and the ionic core Na^{+}. In addition to the static core interaction, the potentials may also include terms for exchange effects and polarization of the core (which includes some form of cutoff parameter to ensure that the polarization term is finite at the origin). Any model potential for sodium that gives rise to a ground state with the correct nodal structure has three unphysical low-lying states that correspond to the $1s$, $2s$, and $2p$ states.

When applying the model potentials for atomic sodium to the effective three-body system e^{+}Na, the model potential is used to describe the interaction of both the electron and the positron with the ion core (with the appropriate sign change). The interaction between the electron and the positron is a simple Coulomb interaction plus a correction to the two-particle polarization potential. It is important to exclude the contribution from the three low-lying states to the electronic part of the three-body wave function.

Ryzhikh *et al.* [1] calculated the binding energy of e^{+}Na using a modified version of the stochastic variational method (SVM) with a model potential. The wave function for the residual ion core was obtained from a Hartree-Fock calculation of the Na^{+} ground state. The Hamiltonian also included a local exchange potential and a projection operator to ensure that the wave function was orthogonal to the ion core. We refer to this model potential as frozen core Hartree-Fock with local exchange (FCHF-LX). The calculations were extended [2,3] to include the effect of dipole polarization and the local exchange term was replaced with the exact exchange interaction (FCHF-EX$_{\mathrm{pol}}$).

There have been three calculations using the adiabatic hyperspherical method (AHM), in which the Schrödinger equation is solved at fixed hyper-radii. An important advantage of this approach is that one can easily eliminate the lowest three potential curves corresponding to the unphysical states. Yuan *et al.* [4] used a model potential that included a static potential obtained from a Hartree-Fock calculation for Na^{+}, a localized exchange potential, and a dipole polarization potential. Han *et al.* [5] carried out an AHM calculation using a different model potential with parameters given by Liu and Starace [6]. They implemented the slow variable discretization method and optimized the distribution of B splines in order to improve convergence. The most recent AHM calculation is that of Le *et al.* [7]. They used the same model potential as in Ref. [1] and explicitly coupled three adiabatic channels corresponding to $\mathrm{Ps}(1s) + \mathrm{Na}^{+}$, $\mathrm{Na}(3s) + e^{-}$, and $\mathrm{Na}(3p) + e^{-}$.

The only other nonadiabatic calculation is that of Kubota and Kino [8], who carried out a coupled-channel calculation using the Gaussian expansion method (GEM). The model potential includes a standard Hartee potential, a local exchange potential, and a dipole polarization potential; a projection operator ensures orthogonality with the core. They explicitly include $e^{+} + \mathrm{Na}(3s)$ and $\mathrm{Ps}(1s) + \mathrm{Na}^{+}$ channels.

It is important to note that the accuracy of the binding energy for e^{+}Na depends on the method, the model potential, and the number of basis functions used to approximate the wave function. The value for α_d has not been directly measured and different values for α_d (ranging from 0.92 to 1.4) have been used in the binding-energy calculations. Since there are no calculations using the exact 11-body Hamiltonian, there exists no rigorous variational bound on the ground-state energy.

The Peach model potential. In our treatment of e^{+}Na, we choose to use the Peach model potential [9]. This potential, which is l independent, is ideally suited for studying effective three-body systems. We have previously used the Peach model potential to calculate the binding energy of e^{+}Li [10] and the positronium formation cross sections for e^{+}-Li collisions just above threshold [11].

The effective potential for the interaction of the electron and the positron with the sodium ion core is given by

$$\begin{aligned} V_{e^-\mathrm{Na}^+}(r_-) = & -\frac{1}{r_-} - \frac{10e^{-\gamma r_-}}{r_-}(1+\delta r_- + \delta' r_-^2) \\ & - \frac{\alpha_d}{2r_-^4}\omega_2(\beta r_-) - \frac{\alpha_q'}{2r_-^6}\omega_3(\beta' r_-), \end{aligned} \tag{1a}$$

$$\begin{aligned} V_{e^+\mathrm{Na}^+}(r_+) = & \frac{1}{r_+} + \frac{10e^{-\gamma r_+}}{r_+}(1+\delta r_+ + \delta' r_+^2) \\ & - \frac{\alpha_d}{2r_+^4}\omega_2(\beta r_+) - \frac{\alpha_q'}{2r_+^6}\omega_3(\beta' r_+). \end{aligned} \tag{1b}$$

(Atomic units are used throughout, unless otherwise stated.) The first two terms in Eq. (1) represent the static potential. The third and fourth terms are the dipole and effective quadrupole contributions to the polarization potential. This is the only calculation for e^+Na to include an effective quadrupole interaction in the model potential. The cutoff function

$$\omega_n(x) = \left[1 - e^{-x}\sum_{i=0}^{n}\frac{x^i}{i!}\right]^2 \tag{2}$$

has the property that $\omega_n(x \to 0) \propto x^{2(n+1)}$. The value for the static dipole polarizability used in the Peach model potential was calculated by Stewart [12] ($\alpha_d = 0.923\,89$) using an uncoupled Hartree-Fock approach and geometric approximation; this value is in reasonable agreement with a later random-phase-approximation calculation by Johnson *et al.* [13] ($\alpha_d = 0.9457$). The values for the other parameters were chosen to provide a fit to the observed spectrum of sodium and to provide the correct nodal structure for the 3s state; they are given in Ref. [14]. The interaction between the electron and positron is given by

$$\begin{aligned} & V_{e^+e^-}(r_+,r_-,r_{+-}) \\ & = -\frac{1}{r_{+-}} + \frac{\alpha_d}{r_-^2 r_+^2}P_1(\hat{r}_+\cdot\hat{r}_-)\sqrt{\omega_2(\beta r_+)\omega_2(\beta r_-)} \\ & \quad + \frac{\alpha_q'}{r_+^3 r_-^3}P_2(\hat{r}_+\cdot\hat{r}_-)\sqrt{\omega_3(\beta' r_+)\omega_3(\beta' r_-)}. \end{aligned} \tag{3}$$

The second and third term are corrections to the two-particle polarization potential, and $P_l(\hat{r}_+\cdot\hat{r}_-)$ is the Legendre polynomial.

Method. To calculate the ground state of e^+Na, we solve the effective-three body Schrödinger equation for $L = 0$ with the finite element method (FEM) [15,16]. In order to accurately approximate the cusps in the wave function at the Coulomb singularities and to enhance convergence, we choose our coordinates to be the distances between particles of opposite charge, r_- and r_{+-}, and $\cos\theta = \hat{r}_-\cdot\hat{r}_{+-}$. Assuming an infinite mass for Na$^+$ and integrating the Schrödinger equation over all space, we obtain

$$\begin{aligned} \iiint \Bigg\{ & \frac{1}{2}\left[\frac{\partial\psi}{\partial r_-} + \frac{r_- - r_{+-}\cos\theta}{r_- r_{+-}}\frac{\partial\psi}{\partial\cos\theta}\right]^2 \\ & + \left[\frac{\partial\psi}{\partial r_{+-}} + \frac{r_{+-} - r_-\cos\theta}{r_{+-}r_-}\frac{\partial\psi}{\partial\cos\theta}\right]^2 \\ & + \frac{1}{2}\left[\frac{r_+}{r_- r_{+-}}\frac{\partial\psi}{\partial\cos\theta}\right]^2 \\ & + \cos\theta\left[\frac{\partial\psi}{\partial r_-} + \frac{r_- - r_{+-}\cos\theta}{r_- r_{+-}}\frac{\partial\psi}{\partial\cos\theta}\right] \\ & \times \left[\frac{\partial\psi}{\partial r_{+-}} + \frac{r_{+-} - r_-\cos\theta}{r_{+-}r_-}\frac{\partial\psi}{\partial\cos\theta}\right] - \frac{(r_{+-} - r_-\cos\theta)}{r_- r_{+-}} \\ & \times \left[\frac{\partial\psi}{\partial r_{+-}} + \frac{r_{+-} - r_-\cos\theta}{r_{+-}r_+}\frac{\partial\psi}{\partial\cos\theta}\right]\left[\frac{\partial\psi}{\partial\cos\theta}\right] \\ & + \psi[V - E]\psi\Bigg\} r_-^2 dr_- r_{+-}^2 dr_{+-} d\cos\theta = 0, \end{aligned} \tag{4}$$

where $r_+ = \sqrt{r_{+-}^2 + r_-^2 - 2r_{+-}r_-\cos\theta}$ and $V = V_{e^-\mathrm{Na}^+} + V_{e^+\mathrm{Na}^+} + V_{e^+e^-}$. The radial coordinates are truncated at $r_-^{\max}$ and $r_{+-}^{\max}$, respectively. The finite three-dimensional coordinate space is divided into rectangular volume elements and the unknown wave function $\psi(r_-,r_{+-},\cos\theta)$ is approximated in each element by a locally defined polynomial basis set. By systematically increasing the number of elements and the values of $r_-^{\max}$ and $r_{+-}^{\max}$, we can achieve the desired level of convergence.

There are three spurious spectra in the solution of Eq. (4) corresponding to states which can be assigned the *approximate* quantum numbers $\psi_{1s}^{\mathrm{Na}}(r_-)\psi_{nl}^{\mathrm{Ps}}(r_{+-}), \psi_{2s}^{\mathrm{Na}}(r_-)\psi_{nl}^{\mathrm{Ps}}(r_{+-})$, and $\psi_{2p}^{\mathrm{Na}}(r_-)\psi_{nl}^{\mathrm{Ps}}(r_{+-})$. The true ground state $\psi_{3s}^{\mathrm{Na}}(r_-)\psi_{1s}^{\mathrm{Ps}}(r_{+-})$ is embedded in these spectra, and the ground-state energy can be nearly degenerate with one or more of these spurious energy levels.

We have developed a method that allows us to calculate only the energy and wave function corresponding to the correct physical ground state. We multiply $V_{e^+\mathrm{Na}^+}(r_+)$ by the scaling factor λ, which we slowly vary from 0 to 1. At $\lambda = 0$, we solve Eq. (4) with Rayleigh quotient iteration using a starting shift $E = E_{3s}^{\mathrm{Na}} + E_{1s}^{\mathrm{Ps}}$ and starting vector $\psi = \psi_{3s}^{\mathrm{Na}}(r_-)\psi_{1s}^{\mathrm{Ps}}(r_{+-})$. (For a discussion of Rayleigh quotient iteration, see Ref. [15].) Although this is not the exact solution (due to three-body terms in the kinetic energy operator), it is an excellent approximation and the solution converges to a tolerance of 10^{-12} in a few iterations. We then gradually increase the scaling factor λ ($\Delta\lambda = 0.1$), using the energy $E(\lambda)$ and the wave function $\psi(\lambda; r_-,r_{+-},\cos\theta)$ from the previous run as a starting shift and starting vector. Rayleigh quotient iteration guarantees *cubic* convergence to the energy and wave function that is closest to the starting eigenpair. Even if the ground-state energy $E(\lambda)$ is nearly degenerate with one of the spurious solutions, the nodal structure of the spurious wave function is dramatically different; by using both a starting shift and vector, we avoid "jumping the track" at these crossings. At $\lambda = 1$, we obtain the true ground-state energy and wave function.

We refer to the implementation of these two techniques—the use of a scaling parameter in the Hamiltonian and the Rayleigh quotient iteration method—as the iterative tracking method (ITM). This method, which avoids the need for a projection operator in the Hamiltonian, is straightforward to implement and could be applied to any problem where one wishes to calculate a particular eigenpair that is embedded in

TABLE I. The binding energy and geometry of e^+Na obtained by various methods, including the present results obtained with FEM-ITM. For each calculation, we identify the model potential (including the value for α_d) and the ground-state energy of Na obtained with that potential.

Method	Potential	E_{Na}	ε	$\langle r_+ \rangle$	$\langle r_- \rangle$	$\langle r_{+-} \rangle$
Experiment [17]		−0.188 858				
SVM [1]	FCHF-LX	−0.181 809	0.000 177	24.00	23.73	3.09
SVM [2]	FCHF-EX	−0.181 801	0.000 161	24.761	24.502	3.086
SVM [2]	FCHF-EX$_{\mathrm{pol}}$ $\alpha_d = 0.99$	−0.188 401	0.000 471	17.253	16.840	3.161
SVM [3]	FCHF-EX$_{\mathrm{pol}}$ $\alpha_d = 0.990$	−0.188 391	0.000 473	17.231	16.818	3.162
AHM [4]	FCHF-LX$_{\mathrm{pol}}$ $\alpha_d = 0.9448$	−0.188 905	0.000 255			
AHM [5]	Liu Starace [6] $\alpha_d = 0.9457$	−0.188 855	0.000 447	17.53	17.12	3.159
AHM [7]	FCHF-LX$_{\mathrm{pol}}$ $\alpha_d = 0.998$		0.000 453			
GEM [8]	FCHF-LX$_{\mathrm{pol}}$ $\alpha_d = 1.369$	−0.188 859	0.000 401	18.25	17.87	3.152
FEM-ITM	Peach [9] $\alpha_d = 0.923\,89$	−0.188 735	0.000 357	18.62	18.24	3.146

a spectrum of states. The only requirement is that one knows the solution at $\lambda = 0$ and that $\Delta\lambda$ is sufficiently small that the energy and wave function can be tracked with the Rayleigh quotient interation method.

Results. We calculate the ground-state energy and wave function for e^+Na by solving Eq. (4) with the FEM; we employ the ITM described previously to isolate the state with the correct 3s electronic structure. The number of elements and the cutoff values for the radial coordinates are systematically increased to obtain the desired convergence. For the results reported in Table I, we use 800 elements with radial cutoff values $r_{+-}^{\max} = 30a_0$ and $r_-^{\max} = 100a_0$; the wave function is approximated by 52 496 local basis functions. We estimate that our energy $E_{e^+\mathrm{Na}}$ is accurate to a few parts in 10^6. In Table I we also include the value of the binding energy $\varepsilon = E_{\mathrm{Ps}} - E_{e^+\mathrm{Na}}$ and the geometry of e^+Na obtained by other methods. One cannot make a direct comparison with other calculations because the model potentials employed are different. For each case, we specify the form of the model potential, the value of α_d, and the value of the ground-state energy of the Na obtained with the potential. All methods verify that the system is bound and that the geometry is consistent with a Ps atom weakly bound to the ion core. One would expect that the binding energy of this weakly bound system would be sensitive to the long-range polarization potential, so the variation in the binding energy obtained with different potentials is not surprising.

In Fig. 1, we show the probability density for the ground state of e^+Na at $\theta = 0$ and $\theta = \pi$. The wave function is only weakly dependent on θ. In Fig. 2, we show a slice through the probability density at $\theta = \pi$, which clearly illustrates the 3s nodal structure of the electronic part of the wave function.

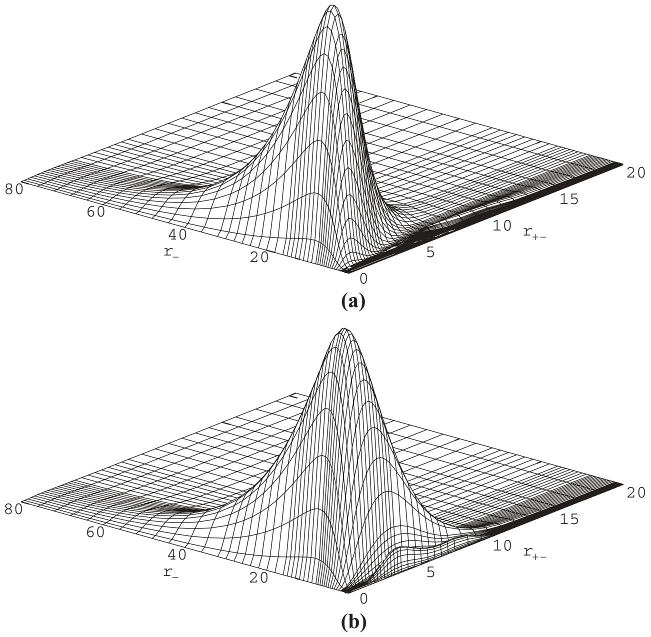

FIG. 1. (a) The probability density $\rho(r_-, r_{+-}, \theta = 0)$; r_- and r_{+-} are given in units of a_0. (b) The probability density $\rho(r_-, r_{+-}, \theta = \pi)$; r_- and r_{+-} are given in units of a_0.

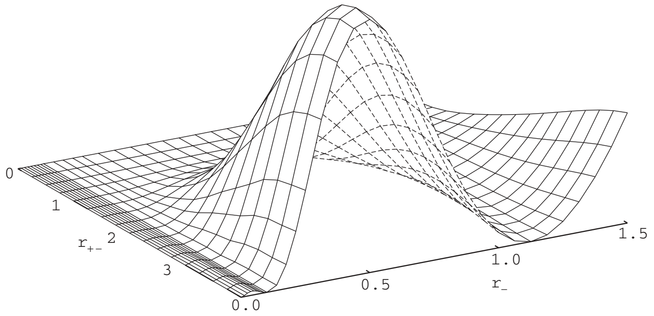

FIG. 2. The probability density $\rho(r_-, r_{+-}, \theta = \pi)$ near the origin, where r_- and r_{+-} are given in units of a_0. The nodal structure is consistent with a 3s electronic state for sodium.

The nodal lines at $r_- \approx 0.1$ and $r_- \approx 1.0$ are consistent with the location of the nodal points for the $3s$ state of the Na atom. There are no nodal lines in the positronic part of the wave function as expected.

Conclusions. We have calculated the energy and geometry of e^+Na by a direct numerical solution (FEM-ITM) of the effective three-body Schrödinger equation. We use the exact, nonadiabatic representation for the three-body kinetic energy operator. The Peach model potential includes both a dipole and an effective quadrupole interaction. The results are consistent with other calculations which have employed different methods and model potentials.

In order to extract the correct physical ground state from a dense spectrum of spurious states, we developed an iterative method that enables us to calculate only the eigenpair of interest. ITM exploits the fact that the energy and the wave function of the desired state are known if the repulsive interparticle interaction is neglected. By slowly "ramping up" the e^+-Na$^+$ interaction with a scaling factor, we can track the desired state using the Rayleigh quotient iteration method. ITM can be used to calculate the ground state of any system involving a model potential where there are low-lying spurious solutions. One could also use the method to calculate a particular excited state (including a doubly excited state [18]) of a three-body system. ITM can be used independently of FEM, although there are particular advantages in combining ITM with FEM.

We are grateful to Drs. Richard Drachman and Gillian Peach for helpful discussions. We acknowledge the UNT Computing and Information Technology Center's High Performance Computing Initiative for providing resources on the Talon HPC cluster.

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