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Laser cooling and the highest bound states of the Na diatom system

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Using a multichannel bound-state method we predict the highest bound states of the ^{23}Na diatom system, which are closely related to the collisional behavior of ultracold atoms. The results agree well with a model where the hyperfine interaction is treated in first-order perturbation theory, except for the triplet level closest to the continuum, which we predict to be very weakly bound. This level is responsible for the large, positive scattering length of the $m_f = \pm f$ states of the lower hyperfine manifold. Its experimental observation would confirm our prediction of a stable Bose condensate.

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Collisions between cold atoms play an important role in the rapidly developing field of laser cooling experiments. They are interesting as a largely unexplored kind of collision in a new temperature regime [1] and are crucial in determining fundamental limits on the accuracy of precision experiments like the cesium atomic frequency standard [2,3], and in determining trapping times in neutral atom traps [4].

Despite rapid recent developments, the description of cold collisions is still far from complete due to insufficient knowledge of interatomic potentials. Fortunately, compared to thermal and superthermal collisions the ranges of energy E and of orbital angular momentum l involved are so small that knowledge of most of the singlet and triplet potentials is not needed: information on the inner potential parts enters collisional observables only in the form of a cumulated radial phase $\phi(E=0,l=0)$ at a rather large radius r_0, together with its first derivatives $d\phi/dE$ and $d\phi/d[l(l+1)]$ at $E=0$, $l=0$ [5–7]. This reduces the needed information considerably: only these parameters and the relatively better known outer potential parts are to be determined.

A second advantage of cold collisions is the possibility, associated with their proximity to the threshold of the continuum, to extrapolate various quantities through threshold both in the upward and downward directions. Information on the highest bound states can be used to derive the scattering lengths [5–7] and vice versa. With this in mind, experimental groups are presently focusing on the determination of the location of such highly excited states by means of two-photon experiments in Li_2 [8], Na_2 [9], and Rb_2 [10]. The present paper is a contribution to this type of approach. Specifically, our purpose is to use a multichannel bound-state method to predict the location and other properties of the highest discrete Na_2 states, which can be used as a guide in the ongoing experiments.

In previous papers [6,7] we have improved the state-of-the-art Na theoretical singlet potential curve by an inverse perturbation analysis (IPA) and obtained bounds on the uncertainty in the inner part of the singlet and triplet potentials, characterized by $\Delta\phi(E=0,l=0)$. From these potentials we derived the scattering length for collisions of Na atom pairs in the $f=1$, $m_f=\pm 1$ states of the lower hyperfine manifold and in the doubly polarized $f=2$, $m_f=\pm 2$ states [11]. The latter was found to be $a_{2,2}=106^{+79}_{-30}a_0$ and the former $a_{1,-1}=86^{+66}_{-23}a_0$. Recently, Ketterle's group at MIT has measured the elastic cross section for collisions of $f=1$, $m_f=-1$ atoms [12]. From the low-energy cross section they find $a_{1,-1}=\pm(92\pm 25)a_0$, in agreement with our prediction. We now proceed, using our present knowledge of the Na+Na interaction properties, to predict the highest Na_2 bound states which have not yet been seen by two-photon spectroscopy or other methods.

The Hamiltonian for the system of two ground-state Na atoms can be written effectively as [13,14]

$$H=\frac{\vec{p}^{\,2}}{2\mu}+\sum_{i=1}^{2} V_i^{hf}+V_i^{Z}+V^{c}, \tag{1}$$

where the first term is the kinetic energy for the relative motion of the atoms with μ the reduced mass, V^{hf} and V^{Z} are the single-atom hyperfine and Zeeman terms, and the two-atom interaction term V^c is the central interaction, i.e., the effective form of the sum of all Coulomb interactions between electrons and nuclei. For the specific form of the above interaction terms we refer to Refs. [13,14]. The central interaction conserves the orbital angular momentum quantum numbers l and m_l and the total spin projection $M_F=m_{f_1}+m_{f_2}$ where $\vec{f}$ is the total one-atom spin vector ($\vec{f}=\vec{s}+\vec{i}$, with $\vec{s}$ and $\vec{i}$ the one-atom electron and nuclear spin, respectively). At large internuclear distances the central interaction can be neglected and the two-atom hyperfine states, denoted as $|\{f_1,m_{f_1},f_2,m_{f_2}\}^+\rangle$, where the + symbol stands for symmetrization, are the most appropriate basis to describe the asymptotic channels in a scattering problem. For small r the central interaction is much stronger than the hyperfine interaction. In this region the basis $|(SI)FM_F\rangle$ is to be preferred. Here, S and I stand for the total (two-atom) electron and nuclear spin quantum numbers, respectively. As most bound-state wave functions do not extend beyond the distance where the exchange part of the central interaction is of the same order of magnitude as the hyperfine interaction, it is usually permitted to neglect the hyperfine interaction. In this paper, however, we are interested in the highest bound levels that do extend to distances where the hyperfine avoided crossings are located and even beyond. An extreme example of the dominant role of the hyperfine mixing in such states has been studied by Demtröder's group [15] for Cs_2,

TABLE I. Positions of Na_2 $l=0$ bound levels. UB stands for "unbound." All energies in cm^{-1}.

Zeroth-order state	E (zeroth order)	E (first order)	E (coupled channels)	$\|v,l(SI)F\rangle$ states
		0.043	0.043	$\|15,0(13)4\rangle$
		UB	UB	$\|15,0(11)2\rangle$
$S=1,v=15,l=0$	-0.002	UB	UB	$\|15,0(11)1\rangle$
		-0.016	-0.016	$\|15,0(13)3\rangle$
		UB	UB	$\|15,0(11)0\rangle$
		UB	-0.077	$\|15,0(13)2\rangle$
$S=0,v=65,l=0$	-0.033	UB	UB	$\|65,0(00)0\rangle$
		UB	UB	$\|65,0(02)2\rangle$
		-0.127	-0.127	$\|14,0(13)4\rangle$
		-0.157	-0.156	$\|14,0(11)2\rangle$
$S=1,v=14,l=0$	-0.171	-0.186	-0.186	$\|14,0(13)3\rangle$
		-0.186	-0.186	$\|14,0(11)1\rangle$
		-0.200	-0.200	$\|14,0(11)0\rangle$
		-0.229	-0.230	$\|14,0(13)2\rangle$
$S=0,v=64,l=0$	-0.458	-0.458	-0.462	$\|64,0(02)2\rangle$
		-0.458	-0.465	$\|64,0(00)0\rangle$
		-0.900	-0.900	$\|13,0(13)4\rangle$
		-0.929	-0.929	$\|13,0(11)2\rangle$
$S=1,v=13,l=0$	-0.944	-0.959	-0.959	$\|13,0(13)3\rangle$
		-0.959	-0.959	$\|13,0(11)1\rangle$
		-0.979	-0.979	$\|13,0(11)0\rangle$
		-1.003	-1.002	$\|13,0(13)2\rangle$
$S=0,v=63,l=0$	-1.723	-1.723	-1.725	$\|63,0(02)2\rangle$
		-1.723	-1.726	$\|63,0(00)0\rangle$

in which case it even leads to a significant amount of mixing of electronic parities g and u. The central interaction couples all two-atom hyperfine states with the same M_F, so that the Schrödinger equation for a scattering or bound-state problem can be formulated as a coupled-channels problem in the hyperfine basis.

Our method of predicting the location and other properties of the multichannel bound states is essentially an extension of a continuum coupled-channels method for cold-atom collisions [13,16] to below threshold. Schrödinger's equation is rewritten as a set of coupled equations

$$-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2}\underline{F}(r)+\underline{C}(r)\underline{F}(r)=E\underline{F}(r), \tag{2}$$

where the columns of the solution matrix $\underline{F}$ represent a complete set of linearly independent solutions and $\underline{C}$ stands for the coupling matrix. The rows correspond to the mutually coupled hyperfine channels. In contrast to the continuum case the (discrete) eigenvalue E is unknown. Guessing a value for E, the set (2) is solved in the outward radial direction up to an interatomic distance beyond the hyperfine avoided crossings, where $\underline{C}$ becomes diagonal. The boundary conditions for the columns of this solution $\underline{F}_{in}$ near the origin are arbitrary as long as they are independent and regular. In the outer region a similar set of equations, decoupled in the hyperfine basis, is solved in the inward direction starting with regular asymptotic bound-state boundary conditions at infinity, yielding a diagonal solution matrix $\underline{F}_{out}$. A necessary and sufficient condition for the existence of a single solution in the internal solution space, which fits smoothly onto one in the outer solution space, is a vanishing Wronskian determinant:

$$\det(\underline{F}_{in}\,\underline{F}'_{out}-\underline{F}'_{in}\underline{F}_{out})=0. \tag{3}$$

This condition is only met at the discrete energies of the bound states. Special care is taken to use a form [17] for the starting conditions as well as for the Wronskian determinant that is of such high order in the radial step size as to be consistent with the order of the radial integration method [1].

Before presenting the results of the coupled-channels bound-state calculation it is instructive to discuss a model in which the hyperfine interaction is treated in first-order perturbation theory. It can be written as

$$V^{hf}=\frac{a_{hf}}{\hbar^2}(\vec{s}_1\cdot\vec{i}_1+\vec{s}_2\cdot\vec{i}_2)=\frac{a_{hf}}{2\hbar^2}\vec{S}\cdot\vec{I}+\frac{a_{hf}}{2\hbar^2}(\vec{s}_1-\vec{s}_2)\cdot(\vec{i}_1-\vec{i}_2)$$
$$\equiv V^{hf}_{+}+V^{hf}_{-}, \tag{4}$$

where $\vec{S}$ and $\vec{I}$ are the total electron and nuclear spin of the two-atom system and a_{hf} stands for the hyperfine constant. The term V^{hf}_{-} mixes singlet and triplet states and can be neglected when the energy spacing between subsequent singlet and triplet levels is large relative to a_{hf}. For V^{hf}_{+} the following expression applies:

$$V^{hf}_{+}=\frac{a_{hf}}{4}[F(F+1)-S(S+1)-I(I+1)]. \tag{5}$$

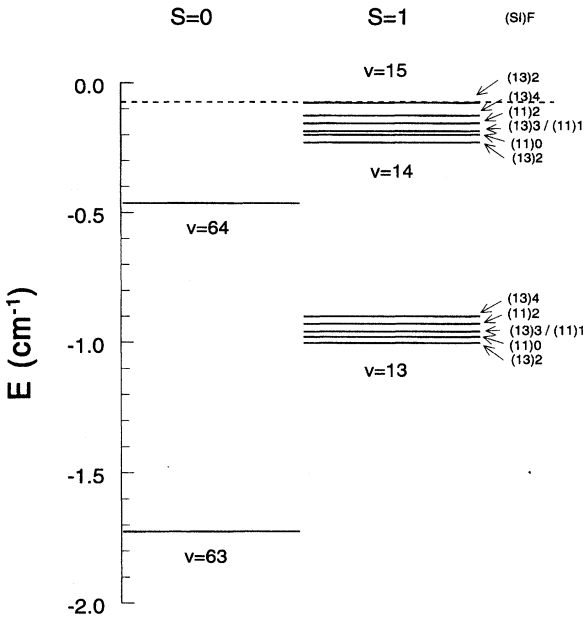

FIG. 1. Positions of Na_2 bound states predicted using the multichannel bound-state method. The dashed line is the onset of the continuum for the channel $(f=1)+(f=1)$. The $|v=15,l=0(13)2\rangle$ level is very weakly bound.

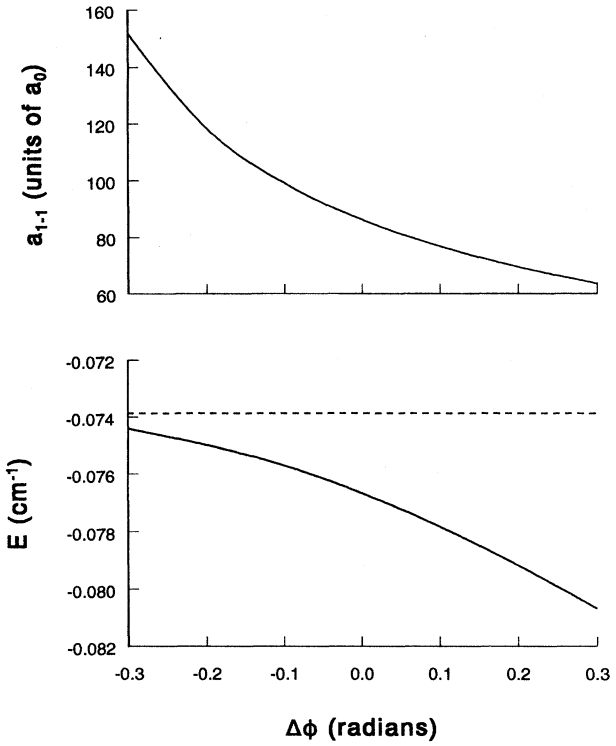

FIG. 2. Energy of $|v=15,l=0(13)2\rangle$ level as a function of added triplet phase, $\Delta\phi(0,0)$ (below) and corresponding scattering length $a_{1,-1}$ (above).

Bose-Einstein statistics requires $S+I+l$ to be even, which makes it easy to derive the bound-state energies from the pure singlet and triplet levels in combination with the hyperfine splittings given by (5). In Table I the results of this first-order calculation and those of a rigorous multichannel calculation are presented for $l=0$. To be specific we restricted ourselves to the case of a vanishing magnetic field. Note the splitting of the $S=0$ levels due to the repulsion by nearby $S=1$ states, which is a consequence of the coupling by V^{hf}_{-} in second order and leads to an effective $\vec{i}_1\cdot\vec{i}_2$ coupling of the nuclear spins [15]. Figure 1 shows the multichannel results. Note the strong "compression" of levels close to the continuum in accordance with the Stwalley–Le Roy–Bernstein formula for long-range molecules [18,19] and the fact that the hyperfine splitting is small relative to the spacing between successive singlet and triplet levels.

From the table it is seen that in almost all cases the rigorous multichannel calculation gives results in close agreement with the first-order predictions. This is especially true for the $F=1$, 3, and 4 states, since V^{hf}_{-} couples only $(SI)F$ states with a common F value. For the above F values, however, only a single (SI) combination is possible.

A remarkable difference between the two calculations is associated with the highest triplet level. The first-order model predicts the $|(13)2\rangle$ state to be in the continuum, whereas the multichannel calculation predicts it to be very weakly bound [20]. Experimental confirmation of this prediction is of crucial importance, since it would confirm the previously predicted [6] positive sign of the scattering length $a_{1,-1}$ needed for the stability of the condensate in ongoing attempts to realize Bose-Einstein condensation in a gas of ultracold $f=1,m_f=-1$ Na atoms [21]. As pointed out above, present experimental evidence has only confirmed the

TABLE II. Energies (in cm^{-1}) of highest Na_2 bound levels.

$\|v,l\ (SI)F\rangle$ state	E	$\|v,l\ (SI)F\rangle$ state	E
$\|14,4(13)4\rangle$	-0.0004	$\|13,7(12)3\rangle$	-0.306
$\|14,4(13)3\rangle$	-0.055	$\|13,7(10)1\rangle$	-0.335
$\|14,4(13)2\rangle$	-0.104	$\|13,7(12)2\rangle$	-0.350
$\|14,3(12)3\rangle$	-0.061	$\|13,7(12)1\rangle$	-0.379
$\|14,3(10)1\rangle$	-0.095	$\|13,6(13)4\rangle$	-0.437
$\|14,3(12)2\rangle$	-0.108	$\|13,6(11)2\rangle$	-0.466
$\|14,3(12)1\rangle$	-0.138	$\|13,6(13)3\rangle$	-0.496
$\|14,2(13)4\rangle$	-0.087	$\|13,6(11)1\rangle$	-0.496
$\|14,2(11)2\rangle$	-0.118	$\|13,6(11)0\rangle$	-0.510
$\|14,2(13)3\rangle$	-0.146	$\|13,6(13)2\rangle$	-0.540
$\|14,2(11)1\rangle$	-0.146	$\|64,6(02)2\rangle$	-0.104
$\|14,2(11)0\rangle$	-0.162	$\|64,6(00)0\rangle$	-0.108
$\|14,2(13)2\rangle$	-0.190	$\|64,5(03)3\rangle$	-0.197
$\|14,1(12)3\rangle$	-0.129	$\|64,5(01)1\rangle$	-0.203
$\|14,1(10)1\rangle$	-0.158	$\|64,4(02)2\rangle$	-0.285
$\|14,1(12)2\rangle$	-0.172	$\|64,4(00)0\rangle$	-0.288
$\|14,1(12)1\rangle$	-0.201	$\|64,3(03)3\rangle$	-0.351
$\|13,8(13)4\rangle$	-0.130	$\|64,3(01)1\rangle$	-0.356
$\|13,8(11)2\rangle$	-0.160	$\|63,11(03)3\rangle$	-0.112
$\|13,8(13)3\rangle$	-0.190	$\|63,11(01)1\rangle$	-0.114
$\|13,8(11)1\rangle$	-0.190	$\|63,10(02)2\rangle$	-0.361
$\|13,8(11)0\rangle$	-0.204	$\|63,10(00)0\rangle$	-0.362
$\|13,8(13)2\rangle$	-0.234		

predicted large absolute value of $a_{1,-1}$ but not its sign.

The above predictions are based on the central values for the singlet and triplet phases $\phi(0,0)$ determined in Refs. [6,7]. The range of uncertainty $\Delta\phi(0,0)$ in these phases obtained in the same work gives rise to an error bar on the positions of the levels. As the uncertainty in the singlet potential is much smaller than that of the triplet potential the predictions for the singlet levels are the most accurate ones. For the highest $S=0$ level, for instance, we find ΔE to be between $+0.013$ and -0.003 cm^{-1}. In Fig. 2 the dependence of the $|v=15, l=0(13)2\rangle$ level on an extra triplet phase $\Delta\phi(0,0)$ is shown together with the corresponding scattering length $a_{1,-1}$. Note the strong increase of the latter for the bound state approaching threshold. A typical error bar for the lower triplet states is ± 0.04 cm^{-1}.

In the foregoing we restricted ourselves to the Na_2 $l=0$ levels. The same multichannel method can be used to predict also the $l\neq 0$ levels, which are of less importance for two-photon experiments initiated with cold atoms. In view of other types of two-photon experiments [22,15] attempting to locate bound states close to the continuum, we also present the energies of the most weakly bound states with $l\neq 0$ (see Table II).

Summarizing, we have predicted the positions of the highest Na_2 singlet and triplet bound states on the basis of a multichannel bound-state method. In general, the differences with a model in which the hyperfine interaction is treated in first order are small. For $l=0$ the highest triplet level forms an exception as our multichannel method predicts the $|v=15,l=0(13)2\rangle$ state to be bound in contrast to the first-order model. Similar deviations from first order are expected on an even larger scale for heavier alkali metals such as Rb_2 and Cs_2.

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[1] B. J. Verhaar, Laser Physics **4**, 1054 (1994).
[2] E. Tiesinga, B. J. Verhaar, H. T. C. Stoff, and D. van Bragt, Phys. Rev. A **45**, 2671 (1992).
[3] B. J. Verhaar, K. Gibble, and S. Chu, Phys. Rev. A **48**, R3429 (1993).
[4] E. Tiesinga, A. J. Moerdijk, B. J. Verhaar, and H. T. C. Stoof, Phys. Rev. A **46**, R1167 (1992).
[5] A. J. Moerdijk, W. C. Stwalley, R. G. Hulet, and B. J. Verhaar, Phys. Rev. Lett. **72**, 40 (1994).
[6] A. J. Moerdijk and B. J. Verhaar, Phys. Rev. Lett. **73**, 518 (1994).
[7] A. J. Moerdijk, B. J. Verhaar, and A. Axelsson, Phys. Rev. A (to be published).
[8] E. R. I. Abraham, W. I. McAlexander, C. A. Sackett, and R. G. Hulet, Phys. Rev. Lett. **74**, 1315 (1995).
[9] P. D. Lett (private communication).
[10] D. J. Heinzen (private communication).
[11] Single-atom spin observables are denoted by lower-case symbols.
[12] K. B. Davis, M. O. Mewes, M. A. Joffe, M. R. Andrews, and W. Ketterle (unpublished).
[13] R. M. C. Ahn, J. P. H. W. v.d. Eijnde, and B. J. Verhaar, Phys. Rev. B **27**, 5424 (1983).
[14] H. T. C. Stoof, J. M. V. A. Koelman, and B. J. Verhaar, Phys. Rev. B **38**, 4688 (1988).
[15] H. Weickenmeier, U. Diemer, and W. Demtröder, Chem. Phys. Lett. **124**, 470 (1986).
[16] J. P. H. W. van den Eijnde, Ph.D. thesis, Eindhoven University of Technology, 1984 (unpublished).
[17] Starting conditions and Wronskian determinant are given by expressions valid up to $O(h^5)$, in accordance with the $O(h^5)$ accuracy of the wave functions after radial integration.
[18] R. J. Le Roy and R. B. Bernstein, Chem. Phys. Lett. **5**, 42 (1970).
[19] W. C. Stwalley, Chem. Phys. Lett. **6**, 241 (1970).
[20] As the $|v=15,l=0,S=1\rangle$ levels are very close to the continuum, we find no d-wave shape resonance. This is consistent with recently obtained photoassociation data in L. P. Ratliff, M. E. Wagshul, P. D. Lett, S. L. Rolston, and W. D. Phillips, J. Chem. Phys. **101**, 2638 (1994).
[21] K. B. Davis, M. O. Mewes, M. A. Joffe, and W. Ketterle, in *Atomic Physics*, edited by D. J. Wineland, C. A. Wieman, and S. J. Smith (AIP, New York, 1995), Vol. 14.
[22] A. M. Lyyra and W. C. Stwalley (private communication).