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Predicting scattering properties of ultracold atoms: Adiabatic accumulated phase method and mass scaling

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Ultracold atoms are increasingly used for high-precision experiments that can be utilized to extract accurate scattering properties. This results in a stronger need to improve on the accuracy of interatomic potentials, and in particular the usually rather inaccurate inner-range potentials. A boundary condition for this short range can be conveniently given via the accumulated phase method. However, in this approach one should satisfy three conditions, two of which are in principle conflicting, and the validity of these approximations comes under stress when higher precision is required. We show that a better compromise between the two is possible by allowing for an adiabatic change in the hyperfine mixing of singlet and triplet states for interatomic distances smaller than the separation radius. Results we presented previously in a brief publication using this method show a high precision and extend the set of predicted quantities. The purpose of this paper is to describe its background. A mass-scaling approach to relate accumulated phase parameters in a combined analysis of isotopically related atom pairs is described in detail and its accuracy is estimated, taking into account both Born-Oppenheimer and Wentzel-Kramers-Brillouin breakdown. We demonstrate how numbers of singlet and triplet bound states follow from the mass scaling.

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I. INTRODUCTION

In 1976 Stwalley [1] suggested the existence of magnetically induced Feshbach resonances in the scattering of cold hydrogen atoms. He pointed out that the specific magnetic field strengths where they occur should be avoided to achieve a stable cryogenically cooled H gas, in view of an enhanced decay at resonance. In 1992 one of the present authors (B.J.V.) and co-workers [2] pointed to a positive aspect of such Feshbach resonances: they allow for an easy control of the interaction strength between *ultracold* atoms, i.e., atoms in the energy range where their interaction is limited to *s* waves. In such circumstances, the interaction strength is characterized by the *s*-wave scattering length *a*. With a Feshbach resonance, the interactions can be tuned from weak to strong and from attractive to repulsive by simply changing an externally applied magnetic field.

Since then these resonances have become an indispensable tool in many successful attempts to control the interatomic interaction, to form ultracold molecules by associating atoms, and to create a superfluid Fermi gas. Feshbach resonances allow experiments with ultracold atoms access to a multitude of the most diverse many-body phenomena [3]. Systematic theoretical work to determine resonant field strengths and scattering lengths for almost all stable alkali metal atoms started immediately after 1992 [4–8] and played a crucial role in the first realizations of Bose-Einstein condensation (BEC) in 1995 [9–11]. An example is presented in Sec. II in connection with the first determinations of scattering lengths. In recent years many experiments have opened the field of ultracold gases with mixed atomic species, where Feshbach resonances continue to be an indispensable tool.

A description of cold collisions between ground-state atoms (and also weakly bound states) requires highly accurate central interaction potentials. Except for the lightest elements (H and Li), *ab initio* potentials do not possess the required accuracy at short range. The slightest change in a potential in that range can easily turn a positive into a negative scattering length, information which is crucial for instance to predict the stability of a BEC.

A way to account for that is to summarize the "history" of the collision for interatomic distances r smaller than a separation radius r_0 by means of a boundary condition on the wave function at r_0, and to determine that condition from a restricted set of available experimental data [4–7]. The basic philosophy of this approach is to give up the goal of extracting the detailed short-range potential as a whole from experiment in favor of a boundary condition with only a few parameters. The boundary condition takes the form of a radial phase of the zero-energy wave function accumulated in the interval $r<r_0$ in either the singlet or the triplet channel, and its energy and angular-momentum derivatives. This presupposes pure singlet and triplet wave functions, which is justified for small interatomic distances where the singlet and triplet states are far enough apart in energy to neglect hyperfine mixing.

Over the years the accuracy of the description of scattering properties obtained with this method has shown a dramatic improvement, keeping pace with the accuracy of the measurements. In this paper we describe an extension of the accumulated phase method, the *adiabatic* accumulated phase method, presented briefly in a previous publication [12]. It is our answer to the need to further increase the accuracy of existing predictions and to predict fundamental quantities such as the strength of the interatomic exchange interaction, the higher dispersion coefficients beyond C_6 or the ferromagnetic or antiferromagnetic nature of spinor condensates.

We start in Sec. II with a brief explanation of notation to be used for the intra-atomic and interatomic interactions.

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Subsequently, we formulate for the first time three conditions that a satisfactory treatment along the lines of the accumulated phase approach should satisfy. It is pointed out that an improved method is called for in view of the fact that two of the conditions become contradictory when more accurate predictions are required. We also introduce some equations for the accumulated phases needed for the later mass scaling and determination of numbers of bound singlet and triplet states. Finally, we point to an essential difference of the method with multichannel quantum defect theory (MQDT) methods. In Sec. III, building on the three explicit conditions of the previous section we present a more sophisticated variant of the accumulated phase method in a more explicit way than was possible in the few lines on that subject in Ref. [12]. We make clear how the approach differs from the conventional one in various interatomic distance ranges. As a further illustration the difference between the approach here with both the old approach and a rigorous calculation is demonstrated by using model potentials. We continue in Sec. IV with a discussion of mass scaling of phase parameters and equations to be used later for the determination of numbers of bound states. In Sec. V sources of inaccuracy for the mass-scaling procedure are discussed, taking into account both Born-Oppenheimer (BO) and Wentzel-Kramers-Brillouin (WKB) breakdown. The resulting uncertainties in our final predictions are compared to the theoretical error bars following from the analysis in Ref. [12]. Section VI compares the r_0 dependences of our predicted interaction quantities for the conventional and adiabatic accumulated phase methods, which gives a further indication of the merits of the approach here. How the numbers of singlet and triplet bound two-atom states can be determined is described and applied in Sec. VII. A summary and outlook are presented in Sec. VIII.

II. INTERACTIONS AND ACCUMULATED PHASE METHOD

A. Two particle Hamiltonian

We consider two like alkali metal atoms in the electronic ground state. They experience a mutual central interaction that can be written as

$$V^{\mathrm{cen}}(r) = V_S(r)P_S + V_T(r)P_T, \tag{1}$$

with $P_{S,T}$ projection operators on the two-atom spin singlet ($S=0$) and triplet ($S=1$) subspaces and r the interatomic separation (note that lower case characters are used to indicate single-atom properties while we reserve capitals for two-atom systems). The singlet and triplet potentials differ by twice the exchange energy $V^{\mathrm{exch}}(r)$ and are at large distances given by

$$V_{S,T} = V^{\mathrm{disp}} - (-1)^S V^{\mathrm{exch}}. \tag{2}$$

The dispersion energy $V^{\mathrm{disp}}(r)$ is described by

$$V^{\mathrm{disp}} = -\left(\frac{C_6}{r^6} + \frac{C_8}{r^8} + \frac{C_{10}}{r^{10}} + \cdots\right), \tag{3}$$

with the dispersion coefficients C_n. An analytic expression for the exchange energy in Eq. (2) has been derived by Smirnov and Chibisov [13] for r values where the overlap of the electron clouds is sufficiently small,

$$V^{\mathrm{exch}} = \frac{1}{2} J r^{7/2\kappa - 1} e^{-2\kappa r}. \tag{4}$$

In this equation J and κ are positive constants with $\kappa^2/2$ the atomic ionization energy; r, J, and κ are in atomic units. The most recent value for J was given by Hadinger *et al.* [14], who made use of Ref. [15].

Leaving out the center-of-mass kinetic energy and including the above interaction the total effective Hamiltonian for two colliding ground-state alkali metal atoms becomes

$$H = \frac{\vec{p}^{\,2}}{2\mu} + \sum_{j=1}^{2} (V_j^{\mathrm{hf}} + V_j^{Z}) + V^{\mathrm{cen}}, \tag{5}$$

in which the first term represents the kinetic energy with μ the reduced mass and $\vec{p}$ the relative momentum operator, while V_j^{hf} is the hyperfine interaction of the valence electron of atom j with its nucleus and V^Z its spin Zeeman interaction.

The hyperfine term can be written as the sum of two parts with different symmetries with respect to interchange of the electronic or nuclear spins,

$$\begin{aligned} V^{\mathrm{hf}} &= \frac{a^{\mathrm{hf}}}{2\hbar^2}(\vec{s}_1 + \vec{s}_2)\cdot(\vec{i}_1 + \vec{i}_2) + \frac{a^{\mathrm{hf}}}{2\hbar^2}(\vec{s}_1 - \vec{s}_2)\cdot(\vec{i}_1 - \vec{i}_2) \\ &\equiv V^{\mathrm{hf}+} + V^{\mathrm{hf}-}. \end{aligned} \tag{6}$$

The convenience of this splitting arises from the fact that $V^{\mathrm{hf}+}$ is diagonal in S, whereas $V^{\mathrm{hf}-}$, being antisymmetric in $\vec{s}_1$ and $\vec{s}_2$, is the part coupling singlet and triplet states.

For the interactions mentioned up to now the total Hamiltonian H is invariant under independent rotations of the spin system and the orbital system around the axis through the overall center of mass parallel to the magnetic field. As a consequence, m_F and the rotational quantum numbers l and m_l are good quantum numbers. Two other, so-called spin-spin interactions, much weaker than the above-mentioned ones, can nevertheless play a significant role in interpreting specific cold atom experiments due to their different selection rules. However, we leave them out of consideration since calculations show their negligible influence in the experiments considered. They are included in our analysis for completeness, but do not turn out to play a significant role in the results, as already pointed out in our brief publication [12].

B. General conditions on separation radius r_0

To make clear what prompted us to introduce the adiabatic variant, it is useful first to formulate three general conditions which the separation radius r_0 has to satisfy for an accumulated phase like approach to be applicable:

(1) r_0 should be so small that in the range $r < r_0$ the lowest $S=0$ and $S=1$ two-atom electron states (see Fig. 1 for a pair of Rb atoms) are sufficiently far apart in energy for the singlet-triplet coupling due to $V^{\mathrm{hf}-}$ to be negligible. This makes it possible to formulate the boundary condition in terms of pure singlet and triplet waves.

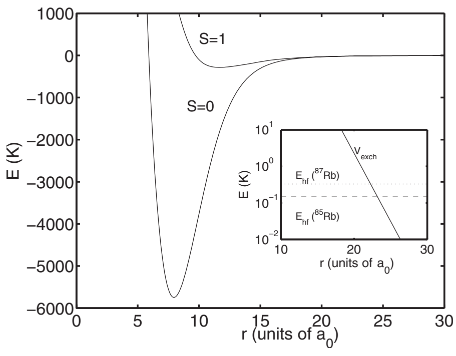

FIG. 1. Main figure: Singlet ($S=0$) and triplet ($S=1$) potentials for a pair of rubidium atoms in the electronic ground state. Inset: $S=0 \leftrightarrow S=1$ energy splitting of two ground-state rubidium atoms (equal to $2V^{\text{exch}}$) versus interatomic separation. The hyperfine energies for the isotopes ^{85}Rb and ^{87}Rb are indicated for comparison.

(2) On the other hand r_0 has to be so large that the singlet and triplet potentials for atomic distances $r > r_0$ can be accurately described by their asymptotic form $V^{\text{disp}} \mp V^{\text{exch}}$ according to Eqs. (3) and (4), with a small number of unknown parameters.

(3) The value of r_0, as well as both the energy E relative to the entrance channel dissociation threshold and the angular momentum l values playing a significant role in the experimental data, should be small enough that a rapidly converging expansion of the $S=0$ and $S=1$ phases in powers of E and $l(l+1)$ is possible, thus also containing a small number of unknown parameters.

Note that the validity of the WKB approximation, which is sometimes mentioned as a condition, is not strictly necessary for the applicability of the approach since the boundary condition at r_0 can in principle be defined in terms of a logarithmic derivative [16]. In the present paper the WKB approximation is only needed for the mass scaling. We devote a discussion of its validity only in that context.

In view of the possibility that these conditions are contradictory, it is far from obvious that a suitable r_0 value can be found. In the first half of the nineties when three U.S. experimental groups attempted to create a BEC in an alkali metal atomic gas, it was possible to predict the signs and (in some cases rough) magnitudes of the scattering lengths for almost all alkali metal species, determining the stability ($a>0$) or instability ($a<0$) of a large BEC. This essential information could already be obtained with the accumulated phase method using rather large values 19 and even $20a_0$ for r_0 (a_0=Bohr radius$=0.5291772 \times 10^{-10}$ m). These large values are compromising condition (1) and therefore also the accuracy of the calculated scattering lengths, however with sufficient accuracy to predict the sign of a. For example, a predicted negative a for ^{85}Rb and a positive a for ^{87}Rb atoms [7] (both spin stretched) led Wieman and co-workers [9] in 1995 to switch from ^{85}Rb to ^{87}Rb in their experiment, leading to the first successful realization of BEC in an ultracold atomic gas.

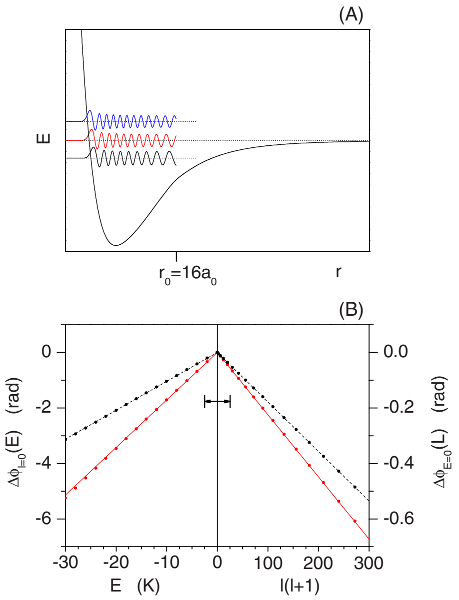

FIG. 2. (Color online) Part A illustrates the behavior of the wave-function phase near $r_0=16a_0$ for three different energies. A comparison between the true accumulated phase (dots) and a first-order approximation (solid lines for triplet, dashed lines for singlet) is shown in part B. As a function of E and $l(l+1)$ the graph shows the difference in accumulated phase $\phi(E,l)$ at $r=r_0$ as compared to the $E=0$, $l=0$ situation: $\Delta\phi(E,0)=\phi(E,0)-\phi(0,0)$ and $\Delta\phi(0,l)=\phi(0,l)-\phi(0,0)$, respectively. The horizontal arrow indicates the typical E and l ranges for which we apply the first-order approximation. Typical rubidium potentials are used for this calculation. Note that for clarity the energy intervals for the wave functions in part A exceed the energies occurring in practice by far.

The concept of an accumulated phase was originally introduced in the spirit of the WKB approximation as the local phase of a rapidly oscillating radial wave function at r_0. Its value $\phi_S(E,l)$ and $\phi_T(E,l)$ for each of the singlet and triplet wave functions is defined by

$$\psi(r_0) = A\frac{\sin[\phi(E,l)]}{\sqrt{k(r_0)}}, \tag{7}$$

and its radial derivative, with up to a constant the singlet or triplet accumulated phase

$$\phi(E,l) = \int^{r_0} k(r)dr. \tag{8}$$

Here $k(r)$ is the local radial wave number for the channel involved,

$$k^2(r) = \frac{2\mu}{\hbar^2}\left[E - V(r) - \frac{\hbar^2 l(l+1)}{2\mu r^2}\right] \tag{9}$$

with μ the reduced mass and $V(r)$ the singlet or triplet potential. With respect to condition (3) earlier in this section we repeat that for (ultra)cold colliding atoms ($T \lesssim 1$ μK) and near-dissociation bound states we are most often considering, E is close to 0 (compared to the depth of the potential at r_0) and l is at most 4. As shown in Fig. 2 for Rb atoms, the small E and l ranges then allow a first-order Taylor expansion for $\phi(E,l)$ according to

$$\phi(E,l) = \phi(0,0) + \frac{\partial \phi}{\partial E}E + \frac{\partial \phi}{\partial[l(l+1)]}l(l+1)$$
$$\equiv \phi^0 + E\phi^E + l(l+1)\phi^l. \tag{10}$$

The generally fractional s-wave vibrational quantum numbers at dissociation, v_{DS} and v_{DT}, are essentially equivalent to the zero-order Taylor terms. They provide for more direct physical insight, however, being a measure of how close the last bound or the first unbound two-atom state is to the dissociation threshold. Their fractional values are defined via interpolation between successive infinite values of the scattering length making use of the radial phase in the deepest part of the potential [4],

$$v_D(\text{mod } 1) = \frac{\phi^0 - \phi^0(a=\infty)}{\pi}, \tag{11}$$

where $\phi^0(a=\infty)$ would be consistent with an infinite value of the scattering length, i.e., a potential which has a bound state at the dissociation threshold. The energy derivatives correspond to the classical sojourn time

$$\tau_{\text{col}} = 2\hbar\, \partial \phi / \partial E \tag{12}$$

of the atoms in the distance range $r < r_0$ for $l=0$ and energies close to threshold. The $l(l+1)$ derivatives are a measure for the influence of the centrifugal force in the rotating two-atom system.

It is very convenient and intuitively appealing to define the boundary condition in the above way. As mentioned above, however, the validity of the WKB approximation is not strictly necessary since the phase $\phi(E,l)$ can be defined in terms of a logarithmic derivative. For $r > r_0$ there is a coupling region where the exchange interaction is of similar magnitude as the hyperfine and Zeeman energies, as indicated in Fig. 1 for the Rb atoms. For larger interatomic distances where V^{exch} has further decreased the two-particle hyperfine states form a good basis.

An advantage of the accumulated phase method compared to alternatives [17–19] is that the above set of phase parameters can be systematically extended by taking more terms in expansion (10) into account. We also point to the difference with MQDT methods in general: in our case the scattering channels are still coupled by the exchange interaction in part of the exterior region $r > r_0$, where V^{exch} is of similar magnitude as the hyperfine energy, as indicated in Fig. 1.

III. ADIABATIC ACCUMULATED PHASE METHOD

The theoretical precision needed for the "state of the art" BEC and Fermi degeneracy experiments forces us to shift r_0 to smaller and smaller atomic distances to neglect the singlet-triplet coupling for $r < r_0$ according to the above-mentioned condition (1) for the applicability of the straightforward accumulated phase method. We then run a real risk of violating condition (2), however. In this section we present a more sophisticated variant of the accumulated phase method, already introduced briefly in Ref. [12], that allows us to relax condition (1) to some extent, making it possible to find a value for r_0 while achieving the desired accuracy.

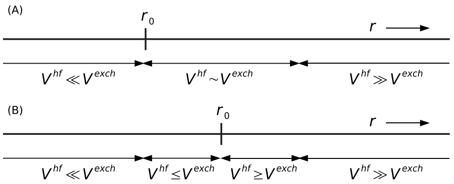

FIG. 3. Subdivision of radial ranges to illustrate choices of r_0. Part A distinguishes three radial ranges. In the left interval S is a good quantum number. In the right interval the individual atomic hyperfine labels f_1, m_{f1}, f_2, m_{f2} characterize the spin states. Conventionally, r_0 is chosen as far right as possible in the $V^{\text{hf}} \ll V^{\text{exch}}$ interval. Part B shows the radial intervals as they occur in the *adiabatic* accumulated phase method. The intermediate radial interval is subdivided in one in which the influence of $V^{\text{hf}-}$ is small and adiabatic and one in which it is not. The separation radius r_0 is chosen as far right as possible in the former interval.

In Fig. 3 we explain the difference between the conventional accumulated phase method and the approach here, distinguishing several intervals along the r axis according to the relative magnitudes of V^{hf} and V^{exch}. In part A we consider three intervals illustrating the conventional method. In the left interval V^{hf} is so weak compared to V^{exch}, i.e., to the $S=0 \leftrightarrow S=1$ splitting of potential curves, that the coupling due to $V^{\text{hf}-}$ can be neglected. We thus have $S=0$ and 1 as a good quantum number. The remaining part $V^{\text{hf}+}$, together with the two-atom Zeeman interaction V^{Z}, can therefore be included effectively in the Hamiltonian via its eigenvalues, which can simply be added to the singlet and triplet potentials, in addition to their centrifugal l splitting. The corresponding basis of spin eigenstates will be referred to in the following simply as $V^{\text{hf}+}$ basis. We thus have a set of singlet and a set of triplet potential curves, each with known energy separations independent of r. In the right interval of part A the situation with respect to the relative magnitude of V^{hf} and V^{exch} is opposite and the individual atomic hyperfine labels f_1, m_{f1}, f_2, m_{f2} characterize the spin states. In the middle interval the two potential terms are comparable. The separation radius r_0 is chosen as far right as possible in the $V^{\text{hf}} \ll V^{\text{exch}}$ interval. The boundary conditions for the pure singlet and triplet radial wave functions at r_0 along the potential curves can therefore be formulated simply in terms of E- and l-dependent pure singlet and triplet phases $\phi(E,l)$.

The insight leading to our alternative approach concerns the role of $V^{\text{hf}-}$. Let us turn to part B of Fig. 3 and consider what happens when we move into the region where $V^{\text{hf}} \sim V^{\text{exch}}$. One will first pass through an interval where the $V^{\text{hf}-}$ coupling is not negligible but still small and adiabatic. In principle, $V^{\text{hf}-}$ induces both a spin mixing between the $S=0$ and 1 states, and a perturbation on the radial wave functions. We include the spin mixing, but neglect the radial perturbation so that the radial functions are still decoupled singlet and triplet waves characterized by pure singlet and triplet accumulated phases. In accordance with the general notion of adiabatic approximation [20] (Eq. XVIII.52), the spin mixing at r_0 is included by means of a rotation in spin space that transforms a spin eigenstate of $V^{\text{hf}+}$ into the corresponding one of V^{hf} and is independent of the potentials left of r_0. Note that the spin mixing is a first-order perturbation, whereas the energy perturbation on the singlet and triplet states is a second-order effect, which we neglect.

As a further illustration of the difference between the two methods and their differences with a rigorous solution we discuss the example of ^{87}Rb+^{87}Rb scattering with initial spin state $|f_1,m_{f1},f_2,m_{f2}\rangle=|1,-1,1,-1\rangle$. We summarize the influence of $V^{\text{hf}-}$ at short range on the solutions of the coupled radial equations for total Hamiltonian (5) in the asymptotic hyperfine basis by means of a local S matrix [21], $\underline{\underline{S}}(r_0)$, that specifies the ratio of the outgoing and incoming parts of the total wave function at r_0. In the vicinity of $r=r_0$, classically accessible so that the local channel wave numbers are real and positive, the radial solutions without $V^{\text{hf}-}$ interaction are given by

$$F_i(r)=\frac{\sin\left(\displaystyle\int_{r_0}^{r}k_i(r)dr+\phi_i\right)}{\sqrt{k_i(r)}},\tag{13}$$

with

$$\phi_i=\phi_{S/T}(E_{\text{tot}}-\varepsilon_i,l_i),\tag{14}$$

the accumulated phases for model singlet and triplet potentials, where the channels i differ from each other by their singlet or triplet character, their l values or their internal energies ε_i. To formulate a local S matrix at r_0 we introduce a complementary solution

$$G_i(r)=-\frac{\cos\left(\displaystyle\int_{r_0}^{r}k_i(r)dr+\phi_i\right)}{\sqrt{k_i(r)}},\tag{15}$$

satisfying the Wronskian condition $W[F_i,G_i]\equiv F_iG_i'-F_i'G_i=1$.

We consider three complete sets of solutions of coupled equations in the asymptotic hyperfine basis in the radial range up to r_0. First, a set of "rigorous" solutions for Hamiltonian (5), containing the total interaction $V^{\text{hf}}+V^{Z}+V^{\text{cen}}$. Near r_0 we transform the solutions to the $V^{\text{hf}+}+V^{Z}+V^{\text{cen}}$ basis and combine them linearly so that the coefficient matrix gets the form

$$\underline{\underline{F}}(r)+\underline{\underline{G}}(r)\underline{\underline{C}},\tag{16}$$

with the $\underline{\underline{F}}$ and $\underline{\underline{G}}$ diagonal matrices having the F and G functions on the diagonal. Second, we have a set for the Hamiltonian with the total interaction $V^{\text{hf}+}+V^{Z}+V^{\text{cen}}$. Transformed to the basis associated with this same interaction, the coefficient matrix near r_0 is simply $\underline{\underline{F}}(r)$, equal to expression (16) without $\underline{\underline{G}}(r)$ term. Finally, we start with the previous set, obtaining $\underline{\underline{F}}(r)$ as a coefficient matrix. However, we then interpret this as a coefficient matrix for the total interaction $V^{\text{hf}}+V^{Z}+V^{\text{cen}}$, which we transform to solutions in the $V^{\text{hf}+}+V^{Z}+V^{\text{cen}}$ basis, and for a suitable set of linear combinations of these solutions the result is a coefficient matrix of the form

$$\underline{\underline{F}}(r)+\underline{\underline{G}}(r)\underline{\underline{C}}^{\text{ad}}.\tag{17}$$

This expression will serve as the boundary condition at r_0 in the adiabatic accumulated phase method. In each of the three cases the coefficient matrix in the original asymptotic hyperfine basis is obtained by the same rotation in spin space transforming the $V^{\text{hf}+}+V^{Z}+V^{\text{cen}}$ eigenstates back into the asymptotic hyperfine states. In contrast to the rigorous C matrix, the adiabatic C^{ad} is model independent, as it depends only on the local adiabatic spin state at r_0. Note that we could have used complex ingoing and outgoing exponentials as basis functions instead of cosine and sine functions. The resulting complex $\underline{\underline{S}}(r=r_0)$ matrix has a simple relation with $\underline{\underline{C}}$.

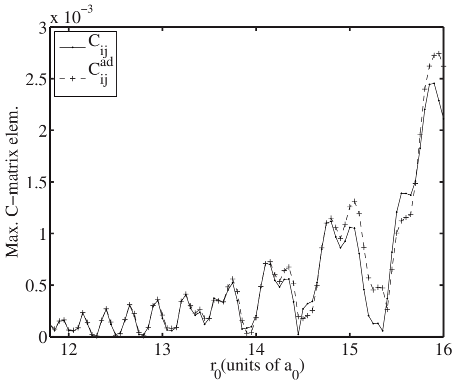

FIG. 4. Comparison of conventional accumulated phase method and alternative approach for ^{87}Rb+^{87}Rb scattering with initial spin state $|f_1,m_{f1},f_2,m_{f2}\rangle=|1,-1,1,-1\rangle$. Solid line: largest C matrix element C_{ij} in absolute value for "rigorous" coupled-channel calculation with r_0 in range $[11.75,16.0]$ a_0. Dashed line: analogous result for C_{ij}^{ad} from adiabatic accumulated phase method. Conventional method corresponds to $C_{ij}=0$

The key question is now how close $\underline{\underline{C}}_{\text{ad}}$ is to $\underline{\underline{C}}$. The solid line in Fig. 4 shows the largest C matrix element in absolute value for r_0 values in the range $[11.75,16.0]$ a_0. The dashed line is the analogous quantity C_{ij}^{ad} from the adiabatic accumulated phase method. Clearly, the latter is in excellent agreement with the "rigorous" result for the small r_0 values. The error gradually grows to 0.25×10^{-3} at $r_0=16.0$ a_0. This amounts to an error of about 10% of the total effect due to $V^{\text{hf}-}$, which by itself is of order 0.4% of the analogous $V^{\text{hf}+}$ quantity $\phi^{E}\times E^{\text{hf}}(^{87}\text{Rb})\sim0.6$. Note that the conventional accumulated phase method corresponds to $C_{ij}=0$. The figure together with the above description illustrates that the adiabatic accumulated phase method is model independent and on the other hand may be expected to follow closely the rigorous behavior.

We emphasize that the approach here includes effectively the adiabatic spin mixing in the complete range $r<r_0$. Although we impose the boundary condition that starts the coupled-channel calculation in the range $r>r_0$ only at r_0, by its local character the adiabatic spin mixing may be understood to have been included for all smaller r values. This is clearly illustrated in Sec. VI, where we discuss an application of the adiabatic accumulated phase method to ^{85}Rb and ^{87}Rb, previously presented in Ref. [12]. It turns out (see column C of Table I in the following) that the deduced potential parameters and v_{DS},v_{DT} are highly independent of r_0 over a rather long range. An important aspect is a comparison with the straightforward accumulated phase method. In

TABLE I. Interaction parameters (a.u.) derived from combined ^{85}Rb and ^{87}Rb experiments (column A) including error bars, mainly due to 10% uncertainty in C_{10}; column B: fractional changes due to phase corrections; column C: percentages of variation in same quantities over range $[10.85,16]$ a_0 of r_0 values according to adiabatic accumulated phase method; column D: same for conventional method.

Quantity	A	B (%)	C (%)	D (%)
$C_6/10^3$	4.703(9)	0.001	0.04	0.1
$C_8/10^5$	5.79(49)	0.002	0.2	0.6
$C_{10}/10^7$	7.665[a]			
$J.10^2$	0.45(6)	3	1	2
$a_T(^{87}\mathrm{Rb})$	+98.98(4)	0.0004	0.001	0.02
$a_S(^{87}\mathrm{Rb})$	+90.4(2)	0.02	0.09	0.2
$a_T(^{85}\mathrm{Rb})$	−388(3)	0.06	0.2	0.3
$a_S(^{85}\mathrm{Rb})$	$+2795^{+420}_{-290}$	0.5	3	7
$v_{DT}(\mathrm{mod}\ 1), n_{bT}(^{87}\mathrm{Rb})$	0.4215(3), 41	0.001	0.03	0.04
$v_{DS}(\mathrm{mod}\ 1), n_{bS}(^{87}\mathrm{Rb})$	0.455(1), 125	0.02	0.07	0.10
$v_{DT}(\mathrm{mod}\ 1), n_{bT}(^{85}\mathrm{Rb})$	0.9471(2), 40	0.002	0.008	0.02
$v_{DS}(\mathrm{mod}\ 1), n_{bS}(^{85}\mathrm{Rb})$	0.009(1), 124	0.5	3	7

[a] Reference [29].

particular, we will present convincing evidence, in addition to Fig. 4, that the variant here allows us to shift r_0 to larger interatomic distances without significant loss of accuracy, thus enabling us to use more reliable potential terms in the range of interatomic distances $r > r_0$ in the form of dispersion and exchange expressions with a small number of parameters.

IV. MASS SCALING: EXPLICIT ISOTOPIC DEPENDENCE OF PHASE PARAMETERS

As long as experimental data are analyzed for bound states and cold collisions of a single pair of (un)like atoms, it is only the local phase at r_0, i.e., the modulo π part of the accumulated phase $\phi(E,l)$ that plays a role in the radial boundary condition. In this section we consider the combined analysis of several isotopic versions of atom pairs and the advantages of mass scaling in that connection. We believe that this subject will play an increasingly important role in cold atom physics, also for collisions of unlike atoms [22]. When analyzing experimental data for two isotopic pairs, making use of the first terms of Taylor expansion (10), we would need to introduce a set of $2(S=0,1)$ times three (ϕ^0, ϕ^E, and ϕ^l) independent parameters for each of the two-atom systems, to be determined by comparing theoretically predicted to experimentally determined properties of cold collisions or weakly bound states.

The mass scaling is based on both the Born-Oppenheimer and WKB approximations. The former approximation enables us to assume equal central potentials for the isotopic pairs. Clearly, it is essential for this approach that Born-Oppenheimer breakdown corrections can be neglected. The WKB approximation makes it possible to use an explicit expression for the accumulated phases as radial integrals containing the reduced mass via the wave number $k(r)$. As we will see, the actual value for r_0 chosen in applications of the adiabatic accumulated phase method is at small enough interatomic distances along the outer slope of the potential wells for the relative atomic motion to provide for an accurate validity of the WKB approximation in the radial range $r < r_0$. We start from WKB integral (8) above, written more specifically as

$$\phi(E,l) = \int_{r_t}^{r_0} k(r)dr + \frac{\pi}{4}, \tag{18}$$

with r_t the inner turning point and the added constant $\pi/4$, associated with the quantum-mechanical penetration into the inner wall of the potential [20] (Chap. VI). We thus have the proportionalities

$$\phi^0 - \frac{\pi}{4} \propto \sqrt{\mu}, \tag{19}$$

and by differentiation of Eq. (18) with respect to E and $l(l+1)$,

$$\phi^E \equiv \left.\frac{\partial \phi}{\partial E}\right|_{l=0} = \int \frac{\mu dr}{\hbar^2 k} \propto \sqrt{\mu}, \tag{20}$$

$$\phi^l \equiv \left.\frac{\partial \phi}{\partial l(l+1)}\right|_{E=0} = \int \frac{dr}{2kr^2} \propto \frac{1}{\sqrt{\mu}}. \tag{21}$$

Clearly, the advantages of a combined analysis of isotopes and the associated mass scaling are (a) we extend the set of available experimental data without increasing the number of fit parameters: we need the phase parameters of only one of the isotope pairs; (b) via the scaling of ϕ^0 the fit becomes sensitive to the number of nodes of the radial wave function left of r_0, in addition to the modulo π part of ϕ^0. With the dispersion+exchange parameters deduced in the analysis we then also know the number of nodes on the right-hand side and thus the numbers of bound singlet and triplet states for all possible isotope pairs, not only those analyzed. We will see an example of this approach in the case of ^{85}Rb+^{85}Rb and ^{87}Rb+^{87}Rb in Sec. VII.

Equations (20) and (21) enable us to mass scale ϕ^E and ϕ^l for two isotopic pairs $\mathcal{A} \equiv A_1, A_2$ and $\mathcal{A}' \equiv A_1', A_2'$ (A_i, A_i' standing for atomic mass numbers) according to

$$^{\mathcal{A}}\phi^E = \mathcal{R}\ ^{\mathcal{A}'}\phi^E \quad \text{and} \quad ^{\mathcal{A}}\phi^l = \mathcal{R}^{-1}\ ^{\mathcal{A}'}\phi^l, \tag{22}$$

where $\mathcal{R} = \sqrt{\mu_{\mathcal{A}}/\mu_{\mathcal{A}'}}$ with μ being a reduced mass. For these scaling equations contributions to $\phi(E,l)$ independent of E and l do not play a role. For the mass scaling of ϕ^0, on the other hand, we have

$$\phi^0 = n_b'\pi + \phi^0_{\mathrm{mod}(\pi)}, \tag{23}$$

with n_b' the number of zero-energy s-wave nodes up to the radius of interest (r_0), excluding the node at $r=0$, and $\phi^0_{\mathrm{mod}(\pi)}$ the modulo π part of the total phase ϕ^0. Each phase cycle π corresponds to one additional radial node and thus an extra (vibrational) bound state in the potential.

Combining this equation with mass-scaling relation (19) we find

$$^{\mathcal{A}}\phi^0_{\mathrm{mod}(\pi)} + {}^{\mathcal{A}}n'_b\pi - \frac{\pi}{4} = \mathcal{R}\left[{}^{\mathcal{A}'}\phi^0_{\mathrm{mod}(\pi)} + {}^{\mathcal{A}'}n'_b\pi - \frac{\pi}{4}\right], \tag{24}$$

so that the scaled $\phi^0_{\mathrm{mod}(\pi)}$ values of the two isotopic pairs are related according to

$$^{\mathcal{A}}\phi^0_{\mathrm{mod}(\pi)} = \mathcal{R}\,{}^{\mathcal{A}'}\phi^0_{\mathrm{mod}(\pi)} + (1-\mathcal{R})\frac{\pi}{4} - {}^{\mathcal{A}}n'_b\pi + \mathcal{R}\,{}^{\mathcal{A}'}n'_b\pi \tag{25}$$

and its inverse, obtained by interchanging the isotopic atom pairs and substituting $1/\mathcal{R}$ for $\mathcal{R}$. The last term gives rise to a number of discrete values for the mass-scaled modulo π phase of isotopic atom pair $\mathcal{A}$, depending on n'_b for the other pair. The interval between these discrete values is $(1-\mathcal{R})\pi$. This discretization can be exploited when extracting information from experimental data of multiple isotopic pairs and requiring the modulo π phases for the pairs considered to be related according to Eq. (25). Clearly, this allows us to deduce ${}^{\mathcal{A}'}n'_b$ and, by exchanging the roles of the isotope pairs, ${}^{\mathcal{A}}n'_b$. It should be emphasized that the (adiabatic) accumulated phase method thus offers a unique possibility to deduce numbers of bound states for potentials *without knowing their short-range part up to* r_0. This approach has been applied in Ref. [12] in the analysis of a set of experimental ^{85}Rb and ^{87}Rb bound state and cold collision data. In the present paper we build on that analysis, which we wish to describe and discuss in more detail. We come back to this in connection with column A of Table I that has been taken from [12]. In the same context we estimate the accuracy of the mass scaling for these isotopes.

We emphasize that the concept of mass scaling as introduced here is basically different from that in other studies of (cold) atom scattering and diatomic bound states (see, e.g., Ref. [23]) in that we apply it to the restricted range $r<r_0$ of interatomic distances thus avoiding the further range, in part of which the central potentials become too shallow to allow for an accurate mass scaling close to the dissociation energy (see the following section).

V. ACCURACY OF MASS SCALING

A crucial issue for the possibility to combine the analysis of different isotope pairs is its expected accuracy. In that connection two types of corrections need discussion, corresponding to the adopted Born-Oppenheimer and WKB approximations.

A. Accuracy of mass-scaling: adiabatic correction to BO

The main correction to the Born-Oppenheimer approximation is the adiabatic or diagonal correction V_{ad} to the interatomic potential [24], given by

$$V_{\mathrm{ad}}(r) = \langle\psi_{\mathrm{el}}(x;r)| - \frac{\hbar^2}{2\mu}\Delta_r|\psi_{\mathrm{el}}(x;r)\rangle \propto \frac{1}{\mu}, \tag{26}$$

with ψ_{el} the electronic wave function (x=electronic coordinates), depending parametrically on the nuclear coordinates. This leads to an adiabatic correction to accumulated phase (18)

$$\phi_{\mathrm{ad}}(E,l) = -\frac{\mu}{\hbar^2}\int_{r_t}^{r_0}\frac{dr}{k(r)}V_{\mathrm{ad}}(r). \tag{27}$$

To show its classical meaning we write it as a time integral over the collision in the classically allowed range within $r_0[dt=dr/v(r[t])]$,

$$\phi_{\mathrm{ad}}(E,l) = -\frac{1}{\hbar}\int_{r_t}^{r_0}V_{\mathrm{ad}}(r[t])dt \equiv -\frac{1}{\hbar}\tau_{\mathrm{col}}\langle V_{\mathrm{ad}}\rangle_{\mathrm{cl}}, \tag{28}$$

proportional to $1/\sqrt{\mu}$. The last member of this equation indicates the proportionality to the collision time τ_{col} and to a classical expectation value in this range. In the following we estimate the isotopic spread ΔV_{ad} and thus the associated spread in accumulated phase parameters on the basis of experiment, on the basis of theory, and using a combination of both.

1. Experimental evidence

In 2000 a paper by Seto *et al.* [25] described a measurement of high-resolution $A\rightarrow X$ emission data for a mixture of the isotopic pairs ^{85}Rb$_2$, ^{87}Rb$_2$, and ^{85}Rb^{87}Rb, covering in total 12 148 transition frequencies. The data allowed a ground-breaking analysis of vibrational level spacings of the $X\ {}^1\Sigma_g^+$ electronic state up to $v=113$ (r up to 25 a_0). Although the data set, with uncertainties ±0.001 cm^{-1}, involved the above three isotopic pairs, the analysis turned out to lead to a common singlet potential without any sign of a Born-Oppenheimer breakdown. A similar analysis for the triplet case does not exist.

This result enables us to deduce an upper limit for the correction to a mass-scaled singlet phase due to Born-Oppenheimer breakdown. To that end we consider the isotopic difference $\Delta\phi_{\mathrm{ad}}(E,l)$ of the adiabatic phase correction and note that the above ±0.001 cm^{-1} uncertainties correspond to quantum-mechanical expectation values of the isotopic difference $\Delta V_{\mathrm{ad}}(r)$ over a large set of rovibrational states v,l with probability densities covering together at least the whole range $[r_t,r_0]$. This justifies the conclusion that the isotopic difference $\Delta V_{\mathrm{ad}}(r)$ is less than 0.001 cm^{-1} in absolute value. For energies E close to 0 and using Eq. (12), we thus find a correction due to the implicit isotopic dependence,

$$|\Delta\phi_S^0| \le 0.001\ \mathrm{cm}^{-1}\phi_S^E = 0.33\times10^{-4}\pi. \tag{29}$$

Here and in the following these estimates apply to the isotopic pairs ^{85,85}Rb$_2-{}^{87,87}$Rb and half these values to the pairs ^{85,85}Rb$_2-{}^{85,87}$Rb and ^{85,87}Rb$_2-{}^{87,87}$Rb. We have used the value of $\partial\phi_S/\partial E\equiv\phi_S^E$ from the analysis in Ref. [12]. In the final result we have split off a factor π representing the basic periodicity associated with the phases ϕ. We expect a similar order of magnitude for the implicit isotopic correction in the triplet case.

2. Theoretical evidence

An order-of-magnitude estimate for both the singlet and triplet case can be based on the long-range expression for V_{ad} proposed by Dalgarno and McCarroll [26],

$$V_{\mathrm{ad}} = -\frac{m_e}{4\mu}\left[V_{\mathrm{BO}} + r\frac{dV_{\mathrm{BO}}(r)}{dr}\right], \tag{30}$$

with m_e the electron mass and $V_{\mathrm{BO}} \equiv V_{S/T}$ the Born-Oppenheimer potential for the atom pair. Assuming that Eq. (30) can be used for an order-of-magnitude estimate in the range $[r_t, r_0]$ [27], we thus obtain

$$\Delta\phi_{\mathrm{ad}}(E,l) = -\frac{m_e}{4\hbar^2}\frac{\Delta\mu}{\mu}\int_{r_t}^{r_0}\frac{1}{k(r)}\left[V(r) + r\frac{dV(r)}{dr}\right]dr. \tag{31}$$

With the singlet potential of Ref. [25] and the *ab initio* triplet potential from Ref. [28] for $r < r_0$, both shifted "vertically" and smoothly joined to dispersion ± exchange forms following from the parameters in Table I for $r > r_0$, we find

$$\Delta_V\phi_S^0 = +0.037 \times 10^{-5}\pi, \quad \Delta_V\phi_T^0 = -0.19 \times 10^{-5}\pi. \tag{32}$$

We note that the smallness of the estimated singlet phase correction is due to the large negative contributions to the radial integral over Dalgarno-McCarroll expression (30) at small r values, which compensate the positive contributions at longer range to a considerable extent.

3. Combined evidence

To improve the above estimates on the basis of experiment and theory together, we note for the singlet case that Dalgarno-McCarroll expression (30) is larger than the maximum adiabatic correction 0.001 cm^{-1} in absolute value allowed by experiment [25] in a range of atomic distances starting from the inner classical turning point $r_t = 5.9a_0$ until $7.7a_0$. We therefore use the experimental limit in radial integral (31) until a distance of $7.7a_0$ so that it fits continuously to the theoretical prediction in the further interval up to the final radius $r_0 = 16a_0$. For the triplet situation r_t is much larger (about $9.5a_0$). In that case the Dalgarno-McCarroll expression is smaller in absolute value than 0.001 cm^{-1} over the whole interval $[r_t, r_0]$. Substituting that in the radial integral, we find our triplet result. In total we find

$$|\Delta\phi_S^0| = 0.61 \times 10^{-5}\pi, \quad |\Delta\phi_T^0| = 0.19 \times 10^{-5}\pi. \tag{33}$$

B. Accuracy of mass-scaling: corrections to WKB

The order of magnitude of this correction is easily estimated by comparing the mass-scaled ^{85}Rb phase parameters to those obtained by numerical integration of the singlet and triplet radial Schrödinger equations up to $r = 16a_0$ for the above-mentioned singlet and triplet potentials with the reduced masses involved. The deviations of the mass-scaled phases are

$$|\Delta\phi_S^0| = |\Delta\phi_T^0| = 2 \times 10^{-5}\pi. \tag{34}$$

Of course, these deviations would rapidly increase beyond $16a_0$, if we were to apply the mass scaling also in that region.

C. Comparison of phase corrections to error bars from analysis in Ref. [12]

To illustrate the smallness of the above estimated phase corrections, we compare them with the error bars obtained in our previous brief description of the adiabatic accumulated phase method in Ref. [12]. In that letter a combined analysis of ^{85}Rb and ^{87}Rb experimental data led to values for interaction and scattering properties of Rb atoms with an unprecedented accuracy. In column A of Table I we recapitulate the dispersion coefficients C_6, C_8, the strength parameter J of the exchange interaction, and the set of pure singlet and triplet scattering lengths + associated fractional vibrational quantum numbers at dissociation v_D, together with their error bars. Column B gives for comparison the maximum fractional changes (in %) of the same quantities that result from the combination of the two types of phase corrections above. We conclude that the latter are small compared to the error bars resulting from the analysis in Ref. [12] and indicated in column A. The latter are mainly due to the 10% error assumed for the theoretical C_{10} value taken from Ref. [29]. The largest of the fractional phase corrections is that for J. We note that that is not unexpected taking into account that this concerns the coefficient of a radially exponential term, which is extremely sensitive to the damping coefficient in the exponential. This also explains the relatively large error bar in column A.

The beautiful agreement with experiment, achieved in the analysis of Ref. [12], is a convincing further indication that the mass-scaling procedure is an excellent approximation. For instance, the values of C_6 and C_8 agree with values $C_6 = 4.691(23) \times 10^3$ [30] and $C_8 = 5.77(8) \times 10^5$ (value obtained via relativistic many-body theory [31] since our brief publication [12]), calculated by Derevianko and co-workers, while J agrees with the most recent calculated value $J = 0.384 \times 10^2$ published by Hadinger and Hadinger [14].

We can also conclude that there is considerable room for an extension of the mass-scaling procedure to applications of the adiabatic accumulated phase method to isotopic pairs of lighter elements than the Rb isotopes studied here, despite the expected larger phase corrections due to Born-Oppenheimer and WKB breakdown.

In this connection it should be emphasized that the concept of mass scaling is formulated here in the sense that it applies to scattering states and weakly bound states, but only in a limited range $r < r_0$ of interatomic distances, thus avoiding the larger distances where the central potentials become too shallow to allow for an accurate mass scaling close to dissociation.

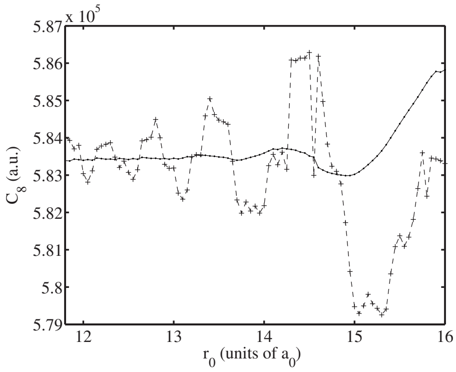

FIG. 5. Predicted value of C_8 versus r_0. The dashed line connects points calculated with the traditional accumulated phase method, the solid curve corresponds similarly to the adiabatic accumulated phase method.

VI. COMPARISON OF ADIABATIC TO CONVENTIONAL ACCUMULATED PHASE METHOD AND DEPENDENCE ON r_0

To illustrate the advantages of our adiabatic accumulated phase method, we compare a calculation including the adiabatic spin mixing at r_0 to one without, i.e., the conventional approach. In both cases we consider the optimization of the accumulated phase and other parameters given a set of ^{85}Rb and ^{87}Rb experimental data according to the analysis in Ref. [12]. It turns out that the optimized values of the quantities in Table I are highly independent of the choice of r_0. To demonstrate that, we have given the percentages of variation over the r_0 interval [10.85, 16.0] in column C of the table. In this case too the exchange strength parameter J is an exception, with a variation of 1%. This can be explained as indicated above in connection with columns A and B of Table I. In column D we have given for comparison the significantly larger percentages of variation in the same quantities according to the conventional accumulated phase method.

In Fig. 5 we show the r_0 dependence of the predicted C_8 as an example. The + signs connected by the dashed curve show the result of a calculation along conventional lines. Each point indicated on the curve represents the outcome of a separate χ^2 optimization. Switching on the spin mixing adiabatically at r_0 gives rise to the solid line. Clearly, the oscillation is strongly reduced. The remaining oscillation is mainly due to the WKB correction and the nonadiabaticity of switching on the coupling due to $V^{\text{hf}-}$.

Even shifting r_0 to $16a_0$ keeps the oscillation amplitude in C_8 at the 0.2% level. Figure 5 suggests that one might just as well select a smaller value for r_0 near $12a_0$ to avoid the $V^{\text{hf}-}$ coupling issue altogether. If we would have done that from the beginning, however, we would have missed a key message from our study: the fact that the final results are highly independent of the central potentials within an interatomic distance of $16a_0$. This applies in particular to the exchange potential V^{exch} for which Smirnov-Chibisov radial dependence (4) is an asymptotic expression. The same applies to asymptotic expression (3) for the dispersion potential.

VII. DETERMINING NUMBERS OF SINGLET AND TRIPLET BOUND STATES FOR ^{85}Rb+^{85}Rb AND ^{87}Rb+^{87}Rb SYSTEMS

Here we come back to the relation between the mass-scaled modulo π accumulated phases for different isotopic versions of a general atom-atom system discussed in Sec. IV, in particular Eq. (25). This relation and its inverse contain the (unknown) numbers of nodes n_b' of the zero-energy radial wave function contained in the potential from the inner turning point up to r_0 for the two interrelated atom pairs $\mathcal{A}$ and $\mathcal{A}'$. As pointed out above, this enables us to deduce the total numbers of bound singlet and triplet states from available experimental data. It is instructive to explain this via the example of the ^{85}Rb+^{85}Rb and ^{87}Rb+^{87}Rb systems, for which an analysis in Ref. [12] led to column A of Table I in that paper, reproduced in Table I. The experimental material analyzed consisted of data on cold collisions and on bound states exceptionally close to the continuum, partly for ^{85}Rb and partly for ^{87}Rb. The six parameters varied in a χ^2 analysis were $^{87}\phi_T^0$, $^{87}\phi_T^E$, $^{87}\phi_T^l$, C_6, C_8, and J, with C_{10} held fixed at the theoretical value from Marinescu *et al.* [29]. This determines the ^{85}Rb phase parameters via mass-scaling relations (25) and (22). Equation (23) then yields the numbers of nodes $^{87}n_b'$ and $^{85}n_b'$ of the ^{87}Rb+^{87}Rb and ^{85}Rb+^{85}Rb triplet s-wave zero-energy radial wave functions up to r_0. The remaining potential parameters being known in the meantime, we can solve the $E=l=0$ radial wave equations beyond r_0 and find the total numbers of nodes and thus the numbers of bound triplet states $n_{bT}(^{85}\text{Rb})$ and $n_{bT}(^{87}\text{Rb})$, given in Table I. The task to find $n_{bS}(^{85}\text{Rb})$ and $n_{bS}(^{87}\text{Rb})$ is different since we can combine the singlet potential of Ref. [25] with the asymptotic potential and directly calculate the total numbers of singlet radial nodes and thus find $n_{bS}(^{85}\text{Rb})$ and $n_{bS}(^{87}\text{Rb})$.

VIII. SUMMARY AND OUTLOOK

We have presented a theoretical method that enables one to describe and predict the interaction and scattering properties of (ultracold) atoms. It allows us, for instance, to predict the ^{87}Rb spinor condensate to be ferromagnetic [12], a prediction for which the relevant scattering lengths have to be calculated with a precision better than 1%. It is also comprehensive: it allows the prediction of a large and varied set of experimental quantities for all pairs of like and unlike atoms. Our results demonstrate that the method allows to extract not only C_6, but also C_8, J, numbers of bound singlet and triplet diatom states, scattering lengths, and even C_{10} and C_{11} from experiment [12]. We have shown that this is accomplished in a model independent way. We repeat that the values extracted agree with theoretical calculations of atomic interaction parameters. In particular, C_8 agrees with the value obtained via relativistic many-body theory as published [31] since our brief publication [12]. All this shows that our method deserves wide application in the analysis of future ultracold atom experiments, for which there is ample opportunity, given the diversity of combinations of scattering and bound-state partners coming into play in experimental groups presently.

Its original version, the accumulated phase method, was designed to predict essential properties such as scattering lengths and Feshbach resonances, enabling the realization of Bose-Einstein condensates and Fermi degenerate gases of alkali metal atoms, for which the short-range interaction was insufficiently known to calculate these properties directly. The method consisted of replacing the short-range interaction with a boundary condition on the two-atom wave function at an interatomic distance $r=r_0$, deducing the boundary condition from available experimental data, and predicting all other relevant data. The *adiabatic* version of the method, described in the present paper, has been presented briefly in a previous letter [12]. Whereas the original method neglected the hyperfine coupling between singlet and triplet states for $r<r_0$ and included this coupling together with asymptotic dispersion+exchange expressions for $r>r_0$, the approach here takes the adiabatic singlet-triplet mixing by V_{hf} into account at the separation radius r_0 and therefore effectively also at smaller r, neglecting the (second-order) changes in the radial waves. This makes it possible to shift r_0 to larger interatomic distances, thus allowing for more reliable asymptotic potential terms in the range $r>r_0$.

We have described a mass-scaling approach to relate the accumulated phases for different isotopic versions of atom pairs. The accuracy of the mass scaling has been discussed, taking into account both Born-Oppenheimer and WKB breakdown. Estimates have been given for the Rb isotopes, pointing to a high accuracy. Again using the Rb isotopes for illustration, the adiabatic and conventional accumulated phase methods were compared, and the r_0 dependence of their optimized interaction parameters was studied. Finally, we have explained how the total numbers of bound singlet and triplet two-atom states follow from a combined analysis of different isotopic versions of atom pairs, without knowing the short-range interatomic interaction.

We believe that the adiabatic accumulated phase method here has great potential to support further studies of cold atom systems, especially in the rapidly growing field of pairs of unlike atoms, to which the method can readily be extended [22]. We would be particularly interested in investigating the influence of an external electric field. We already mentioned above the present experimental and theoretical activities in the field of the scattering and bound states of identical Cs atoms [32]. The set of phase parameters that our approach makes use of can be systematically extended when larger energy or angular-momentum ranges come into play experimentally, contrary to other choices used for the adjustment of the short-range part of model potentials [17–19]. We believe that this attractive aspect of our method, which is intimately connected with its model independent features, will play a favorable role in future work.

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