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Adiabatic approximation and the other (lower) bound on the scattering length

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The static approximation, which neglects the distortion of the (complex) target, that is, virtual excitations, during the collision of a particle with the target, was shown previously to give an *upper* bound on the scattering length when the number of bound states supported by the static and true Hamiltonians are the same. It represents an underadjustment of the target to the field of the scattering particle. It is perhaps then to be expected that the adiabatic approximation, in which the target wave function is calculated for each value of the incident particle coordinate as if the incident particle were fixed at the given point and which represents therefore an overadjustment of the target to the field of the incident particle, might provide the opposite bound, the *lower* bound, on the scattering length. This possibility is explored for the determination of scattering lengths. The bound property is shown to hold in cases where both the true and adiabatic Hamiltonians support the same number of bound states; some (reasonable) subsidiary conditions must also be satisfied. Possible extensions of the formulation to scattering with nonzero energy and with exchange are briefly mentioned. The theory is then applied to e^+H and e^+He scattering at zero incident energy; a reasonably accurate bound for the latter system is obtained, but the adiabatic approximation gives only a very crude, though rigorous, bound on the e^+H scattering length. A connection between the generalized optical potential and the adiabatic potential is derived using projection-operator techniques, thus further clarifying the physical content of the adiabatic picture. Bounds are also obtained for atom-atom and ion-atom collisions; they are interesting only if the electron-proton mass ratio is not thought of as vanishingly small. Some consideration is given to pH scattering. Lower bounds on electron-atom scattering lengths are more difficult to obtain.

I. INTRODUCTION

The reason that it is possible to so readily obtain a (Rayleigh-Ritz) variational upper bound on the lowest (discrete) energy eigenvalue of a system is precisely because it is the lowest state of the total Hamiltonian H. Similarly, the possibility of developing such a simple form[1] for the variational upper bound on the scattering length A for the scattering of system C by system D, when $C+D$ cannot form a composite bound state, is precisely because we are then once again concerned with the lowest eigenvalue of H, even if it is here at the edge of the continuum spectrum. The determination of an upper bound on A when bound states of $C+D$ exist,[2,3] and the determination of one bound on the phase shift[4] and, more generally, on certain elements of the reaction matrix[5] proceeds by reformulating the problem in such a way that H is replaced by an effective Hamiltonian whose eigenvalues all lie above the total energy of the incident particle plus target in the scattering problem under consideration. [It is clear that the bound on the ground-state energy will be an upper bound, since the trial function is necessarily a superposition of states with the correct and with higher energies. The nature of the bound on scattering lengths, phase shifts, and scattering parameters in general, that is, whether the bound on a given scattering parameter is an upper or lower one, is a matter of convention, depending upon the definition of that scattering parameter. With the standard definitions, it follows from comparing the effective range theory expansions of $k^{2L+1}\cot\eta_L$, where L is the angular momentum, η_L is the phase shift, and k is the wave number, that

$$1/A = +\kappa + \cdots ;$$

this assumes that there exists one or more bound states of H, one of which is a very weakly bound state with energy $-\hbar^2\kappa^2/2m$. Since the Rayleigh-Ritz method provides a lower bound on $\kappa > 0$, it follows that the "analogous" bound on A will be an upper bound. Furthermore, for very small k, the standard definitions—there is some lack of conformity here—lead to

$$\eta(\bmod \pi) = -kA .$$

The analogous bound on η will therefore be a lower bound, and the bound on $\cot\eta$ will be an upper bound.]

From the above discussion, it is to be expected that the determination of the other bound on discrete eigenvalues or on scattering parameters will be a rather more difficult matter, since the spectrum of H is not bounded from above. This is indeed the case; results for the other bound that have been obtained[6-10] are either very complicated because they depend upon the operator H^2, or they are rather specialized, requiring for example that various potentials be everywhere repulsive.[11] In this paper we will explore an approach which will be much more general than the latter approaches and which can be much simpler to apply than the former.

We begin by noting that there is an alternative way of viewing the usual bound, the upper bound on the energy or the scattering length, and the lower bound on the phase shift, for example. Thus, for both bound states and scattering problems, the objective is to make the potential as effective as possible, that is, in the first case to lower the energy and in the second to draw in the wave function and thereby increase the phase shift. Consider for example the scattering of a distinguishable particle by a target under conditions such that only elastic (single-channel) scattering is possible; we assume that the target ground-state wave function is known. Then it has been shown that the (exact numerically obtainable) static-approximation phase shift η_{stat} represents a bound on the true phase shift η. In the static approximation, the target is assumed to be frozen in its ground state during the scattering process, that is, the incident particle does not affect the target though it is itself affected by, and thereby scattered by, the target. More generally, the close-coupling approximation, a direct extension of the static approximation, in which the target is allowed to be in its ground state or in one of a finite and specified set of excited states, also provides a numerically obtainable bound on η. Furthermore, as the set is expanded, the phase shift estimate monotonically approaches the correct η. The formal proof proceeds[4,5] by comparing the effective one-body potentials that the particle sees in the static approximation, in successive close-coupling approximations, and in the exact case. Though some of the effective one-body potentials can only be obtained formally, it is still possible to prove rigorously that they decrease monotonically as the true problem is approached. The "physical" interpretation of these results is that we are allowing more and more of the effect of the interaction to be properly taken into account, that is, that we are enabling the target to adapt itself better and better to the effects of the field generated by the incident particle.

In the light of the above remarks, it is natural to ask whether one can introduce an approximation in which the adaptation of the target is *greater* than that which actually occurs, and whether such an approximation would provide the other bound on the various scattering parameters under consideration. The adiabatic approximation is one such candidate.[12] In an actual problem, the response of the target to the particle stimulus is effectively determined by a time-dependent response function, since the particle is in motion; in the adiabatic approximation the response of the target for the projectile particle at a particular position is calculated as if the particle were fixed at the given position, and the target is allowed to possibly overadapt to the effect of the particle. The effective potentials generated in this way may then provide opposite bounds on scattering parameters and binding energies. Various quantities which are being bounded are listed in Table I.

It must be emphasized that a bound provided by the adiabatic approximation need by no means be a purely formal result, since the adiabatic approximation can provide a much simpler scattering problem than the original one. We formulate the procedure for obtaining bounds on A in Sec. II in the adiabatic approximation. Section III contains additional discussions on the adiabatic picture based on two slightly different choices of the adiabatic Hamiltonian. Although the basic structure of the operators involved is quite different, the resulting amplitudes are essentially the same as those derived in Sec. II. A brief discussion on the explicit angular momentum decomposition is given in Sec. IV, and Sec. V con-

TABLE I. Quantities to be bounded, and theoretical approaches that generate upper and lower bounds, and upper and lower variational bounds (minimum and maximum principles). Quantities to be bounded, defined so that a given approach leads to the same kind (upper or lower) of bound or variational bound: (1) binding energy: E_B; (2) scattering length: A_L; (3) negative of scattering length phase[a]: $-\gamma=\tan^{-1}A$; (4) negative of phase shift: $-\eta_L$; (5) $k^{2L+1}\cot\eta_L$; (6) negative of eigenphase shifts: $-\eta^{(i)}$ (i is the channel index); (7) diagonal elements of the inverse reactance matrix[b]: $(K^{-1})_{ii}$; (8) Linear combinations of the inverse reactance matrix[b]: $\sum_{ij} a_i K_{ij}^{-1} a_j$; ($a_i$ specifies the initial condition in channel i).

Upper bounds and minimum principles	Lower bounds and maximum principles
Static approx.[c]	Adiabatic approx.[d]
Close-coupling approx.[c]	Adiabatic close-coupling approx.[e]
QHQ operator[c]	$(QHQ)^2$ operator[f]
H^2-type operators[g,h]	H^2-type operators[g,h]
$V<0$ case[i]	$V>0$ case[j]

[a] Reference 13.
[b] Reference 5.
[c] References 2–4.
[d] Present paper.
[e] Reference 26.
[f] References 8–10.
[g] Reference 6.
[h] Reference 7.
[i] Reference 8.
[j] Reference 11.

tains several applications of the bounds. Appendix A contains some formal results on the adiabatic potential, and Appendix B contains a discussion of some of the effects of symmetry, particularly with regard to proton-hydrogen scattering. Much of the material in Sec. V can be understood after having read through Sec. II A.

II. LOWER BOUNDS ON SCATTERING LENGTH

We restrict our consideration to scattering problems for which the incident relative kinetic energy is zero and for which elastic scattering is the only possible process. To simplify the discussion, we will talk of the scattering of an incident particle with no internal structure by a neutral target; prototype problems include, for example, positrons on hydrogen or helium atoms. (We ignore the possibility of annihilation.) With $T(\vec{R})$ the kinetic-energy operator of relative motion and $V(\vec{r},\vec{R})$ the target–incident-particle interaction, the Hamiltonian H of the system is given by

$$H(\vec{r},\vec{R}) = H_T(\vec{r}) + T(\vec{R}) + V(\vec{r},\vec{R}) , \qquad (2.1)$$

where $\vec{r}$ denotes the internal variables of the target system and $\vec{R}$ denotes the coordinate of the incident particle with respect to the atomic nucleus. (Here we ignore corrections of the order of m_e/M_p, where m_e is the electron mass and M_p is the nuclear mass.) The target Hamiltonian H_T has eigenfunctions ψ_{Tn} and eigenvalues E_{Tn}, where

$$H_T(\vec{r})\psi_{Tn}(\vec{r}) = E_{Tn}\psi_{Tn}(\vec{r}) , \qquad (2.2)$$

$$(\psi_{Tn}, \psi_{Tm}) = \delta_{nm} . \qquad (2.3)$$

(In the following, we omit the subscript L on $\Psi_{L,ad}$ and $H_{L,ad}$ whenever no ambiguity arises.) The scattering process to be studied is defined by

$$(H - E_{T0})\Psi(\vec{r},\vec{R}) = 0; \qquad (2.4)$$

only for purposes of discussion, we will assume here and later that the target ground-state wave function has zero total angular momentum $l = 0$. The boundary conditions on Ψ are then given by

$$\Psi(\vec{r},\vec{R}) \to \left(\frac{M_{\text{red}}}{2\pi\hbar^2}\right)^{1/2} \psi_{T0}(\vec{r}) \times \left(R^L - \frac{A_L}{R^{L+1}}\right) P_L(\hat{R}\cdot\hat{k}), \quad R \to \infty \qquad (2.5)$$

$$\Psi(\vec{r},\vec{R}) \to 0, \quad r \to \infty ,$$

where M_{red} is the reduced mass, the incident momentum $\hbar\vec{k}$ is along the z axis, and Ψ is regular at $r = 0$ and at $R = 0$. We are concerned here with scattering in a state of total angular momentum L. The subscript L will often be understood and we will from now on often simply write A rather than A_L; as noted above, the subscript L will also often be understood in connection with various wave functions and Hamiltonians.

In seeking a lower bound on A, it will be useful to consider a different scattering system defined by a Hamiltonian H_t, to be specified in detail later, with the continuum threshold also at E_{T0}. The associated zero-incident-energy wave function Ψ_t is defined, for a given value of L, by

$$(H_t - E_{T0})\Psi_t = 0 , \qquad (2.6)$$

and by the boundary condition (2.5) but with A replaced by A_t. A simple manipulation of Eqs. (2.4) and (2.6) and use of the boundary conditions gives, for any L,

$$A = A_t + (\Psi_t, (H - E_{T0})\Psi_t) - (\delta\Psi, (H - E_{T0})\delta\Psi) , \qquad (2.7)$$

where

$$\delta\Psi \equiv \Psi_t - \Psi . \qquad (2.8)$$

The form (2.7) was used earlier[1,2] to derive bounds and variational bounds on A; for example, by choosing H_t to be the static Hamiltonian

$$H_t = H_{\text{stat}}(\vec{r},\vec{R}) = H_T(\vec{r}) + T(R) + V_{00}(R) , \qquad (2.9a)$$

where

$$V_{00}(R) = \int d\vec{r}\, |\psi_{T0}(\vec{r})|^2 V(\vec{r},\vec{R}) , \qquad (2.9b)$$

and assuming that the incident particle and the target cannot form a bound state, that is, that H cannot support a bound state, it was found that

$$A \leq A_{\text{stat}} , \qquad (2.10)$$

where A_{stat} is the scattering length associated with $T + V_{00}$. [More generally,[3] Eq. (2.10) is valid if H and H_{stat} support the same number of bound states.]

Since we are now seeking the *opposite* lower bound on A, it will not be unnatural to interchange the roles of H and H_t, and consequently of Ψ and Ψ_t and of A and A_t, and rewrite Eq. (2.7) as

$$A_t = A + (\Psi, (H_t - E_{T0})\Psi) - (\delta\Psi, (H_t - E_{T0})\delta\Psi) . \qquad (2.11)$$

We now have $\delta\Psi = \Psi - \Psi_t$, but since $\delta\Psi$ appears quadratically in Eq. (2.11) the change in sign has no effect and we will continue to use Eq. (2.8). Further, in utilizing (2.11), we expect it to be useful to associate H_t with the adiabatic approximation. The adiabatic picture of the scattering process as described in Sec. I may be formulated in terms of the distorted target states generated for each value of $\vec{R}$ by $H_T + V$,

$$[H_T(\vec{r}) + V(\vec{r},\vec{R})]\,\phi_n(\vec{r};\vec{R}) = \mathcal{E}_n(R)\phi_n(\vec{r};\vec{R}) . \qquad (2.12)$$

The eigenfunctions ϕ_n satisfy the orthonormality conditions

$$\int \phi_n^*(\vec{r};\vec{R})\phi_m(\vec{r};\vec{R})\,d\vec{r}=\delta_{nm}\quad\text{for each } \vec{R}\,, \tag{2.13a}$$

and the boundary conditions

$$\phi_n(\vec{r};\vec{R})\to\psi_{Tn}(\vec{r})\,,\quad R\to\infty\,. \tag{2.13b}$$

(A given ϕ_n does not have a well-defined value of the angular momentum. In Sec. IV, we consider an alternate approach in which the analogue of ϕ_n does have a well-defined value of the angular momentum.) The eigenvalues $\mathcal{E}_n(R)$ satisfy

$$\mathcal{E}_n(R)\equiv E_{Tn}+\mathcal{V}_n(R)\to E_{Tn}\,,\quad R\to\infty\,; \tag{2.13c}$$

Eq. (2.13c) defines $\mathcal{V}_n(R)$. Some detailed properties of $\mathcal{V}_n$ and ϕ_n are described in Appendix A. In particular, we note here that $\mathcal{V}_0(R)$ represents the lowest energy of interaction of the target and the projectile for the projectile fixed at $\vec{R}$ and the target adjusting itself to this fixed external perturbation. The Pauli principle is to be fully accounted for. For e^+-He scattering, for example, $\phi_n(\vec{r};\vec{R})$ would have to be antisymmetric under the interchange of the coordinates of the electrons. (Section VI contains a brief comment on the possibility of obtaining lower bounds on e^--atom scattering lengths, a possibility that is not considered in the present section.)

The above discussion suggests that a good candidate for H_t is

$$H_t=H_{ad}=(T+\mathcal{V}_0+E_{T0})1 \tag{2.14a}$$

or

$$H_t(\vec{r},\vec{R})=H_{ad}(\vec{r},\vec{R})\equiv[T(\vec{R})+\mathcal{V}_0(R)+E_{T0}]\,\delta(\vec{r}-\vec{r}\,')\,. \tag{2.14b}$$

This choice is by no means unique. In fact, though it is in some senses the simplest choice there are some difficulties associated with the presence of the unit operator 1 and the consequent lack of specification of the state of the target. Alternative choices of H_{ad} that do not suffer from this last defect are discussed in Sec. III.

We now consider the consequences of the choice (2.14). By (2.12) we have

$$H_T(\vec{r})+V(\vec{r},\vec{R})-\mathcal{E}_0(R)\geq 0\quad\text{for all } \vec{R} \tag{2.15}$$

for quadratically integrable functions of $\vec{r}$. (In all operator inequalities, quadratic integrability in the appropriate variables will be understood.) It follows from the definitions (2.1) of H and (2.14) of H_{ad}, using (2.13c) and (2.15), that, for functions of $\vec{r}$ and $\vec{R}$ that are quadratically integrable in $\vec{r}$,

$$H(\vec{r},\vec{R})\geq H_{ad}(\vec{r},\vec{R}),\quad\text{for all } \vec{R}. \tag{2.16a}$$

This inequality remains valid if we project onto the subspace of given total angular momentum L. We then have, for quadratically integrable functions of $\vec{r}$,

$$H_L(\vec{r},\vec{R})\geq H_{L,ad}(\vec{r},\vec{R})=\left(t_R+\frac{L(L+1)\hbar^2}{2M_{\text{red}}R^2}+\mathcal{V}_0(R)+E_{T0}\right)\delta(\vec{r}-\vec{r}\,')\,, \tag{2.16b}$$

where

$$t_R\equiv-\frac{\hbar^2}{2M_{\text{red}}}\frac{1}{R^2}\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R}\,. \tag{2.16c}$$

This inequality suggests that we are on the right track. We define the scattering wave function in the adiabatic approximation Ψ_{ad} as the solution of

$$[H_{ad}(\vec{r},\vec{R})-E_{T0}]\Psi_{ad}(\vec{r},\vec{R})=0\,, \tag{2.17}$$

subject to the boundary condition

$$\begin{aligned}\Psi_{ad}&\to(M_{\text{red}}/2\pi\hbar^2)^{1/2}\psi_{T0}(\vec{r})\\&\quad\times[R^L-(A_{L,ad}/R^{L+1})]P_L(\hat{R}\cdot\hat{k})\,,\quad R\to\infty\\\Psi_{ad}&\to 0\,,\quad r\to\infty\,.\end{aligned} \tag{2.18}$$

We then have

$$\Psi_{ad}(\vec{r},\vec{R})=\psi_{T0}(\vec{r})u_{ad}(R)P_L(\hat{R}\cdot\hat{k})\,, \tag{2.19}$$

where

$$\{t_R+[L(L+1)\hbar^2/(2M_{\text{red}}R^2)]+\mathcal{V}_0(R)\}u_{ad}(R)=0\,. \tag{2.20}$$

Note that there are solutions of (2.17) of the form $\psi_{Tn}(\vec{r})u_{ad}(R)P_L(\hat{R}\cdot\hat{k})$for $n\neq 0$, but that these solutions must be discarded because of the boundary conditions (2.18). A slightly different and somewhat less artificial formulation of the problem in which this complication—the appearance of unwanted solutions which must be discarded—does not appear is presented in Appendix A and Sec. III.

With the choice (2.14), Eq. (2.11) becomes

$$A_{ad}=A+(\Psi,(H_{ad}-E_{T0})\Psi)-(\delta\Psi,(H_{ad}-E_{T0})\delta\Psi)\,, \tag{2.21}$$

where, by (2.8),

$$\delta\Psi\equiv\Psi_{ad}-\Psi\,. \tag{2.22}$$

Equation (2.21) represents one starting point in an attempt to obtain a lower bound on A. We begin by using (2.4) and (2.16) to give

$$(\Psi,(H_{ad}-E_{T0})\Psi)=(\Psi,(H_{ad}-H)\Psi)\leq 0\,. \tag{2.23}$$

It follows that

$$A_{ad}\leq A-(\delta\Psi,(H_{ad}-E_{T0})\delta\Psi)\,. \tag{2.24}$$

We will have to make some specific assumptions to proceed further.

A. H_{ad} cannot support a bound state

We assume that H_{ad} is not strong enough to support a bound state. Formally, we then have

$$H_{ad} - E_{T0} \geqslant 0 ,$$

with respect to any quadratically integrable function of $\vec{R}$ and $\vec{r}$, or,[1] with respect to functions which can be thought of as the limits of quadratically integrable functions. One example of the latter class of functions is $\delta\Psi$ for $L = 0$, which behaves asymptotically as

$$\delta\Psi \to (M_{\text{red}}/2\pi\hbar^2)^{1/2}\psi_{T0}(\vec{r})(A - A_{ad})/R, \quad R \to \infty . \tag{2.25}$$

[For $L > 0$, the $\delta\Psi$ that corresponds to (2.25) falls off as R^{-L-1} and thus is always square integrable.] We therefore have

$$(\delta\Psi, [H_{ad} - E_{T0}]\,\delta\Psi) \geqslant 0 . \tag{2.26}$$

{Note that Ψ is neither quadratically integrable nor the limit of a quadratically integrable function and it does *not* follow that $(\Psi, [H_{ad} - E_{T0}]\Psi)$ is positive; on the contrary, as we saw in (2.23), it is negative.} The use of Eq. (2.26) in (2.24) gives the sought for *lower* bound

$$A_{L,ad} \leqslant A_L \tag{2.27}$$

if $H_{L,ad}$ cannot support a bound state. Note that we have obtained this result without the use of the difficult operator H^2 which arose previously[6-10] in lower-bound studies.

The knowledge that H_{ad} cannot support a bound state would necessarily have to be arrived at theoretically. Note that H cannot support a bound state if H_{ad} cannot.

B. H and H_{ad} can each support one and only one bound state

We now assume that H_{ad} can support one and only one bound state, that is, in $\vec{R}$ space only, $T(\vec{R}) + V_0(R)$ has one and only one negative eigenvalue. It follows that H can support at most one bound state (in the full $\vec{r}$ and $\vec{R}$ space). We assume that H can in fact support one bound state; a knowledge of the number of bound states supported by H could be arrived at theoretically or experimentally. Let the true bound-state wave function be $\Psi_B(\vec{r}, \vec{R})$, where

$$H\Psi_B = E_B\Psi_B, \quad (\Psi_B, \Psi_B) = 1 . \tag{2.28}$$

By assumption, we have $E_{T0} < 0$ and $E_B < E_{T0}$; the latter inequality is just the statement of the existence of a composite bound state. We therefore have

$$0 > E_{T0} > E_B = (\Psi_B, H\Psi_B) \geqslant (\Psi_B, H_{ad}\Psi_B); \tag{2.29}$$

the last step follows from (2.16).

We now go further and write

$$(P\Psi_B, (H_{ad} - E_{T0})P\Psi_B) \leqslant (P\Psi_B, (H - E_{T0})P\Psi_B) < 0 , \tag{2.30a}$$

where $P = \psi_{T0}\rangle\langle\psi_{T0}$ is the projection operator on to the target ground state. The first inequality follows from the fact that $H_{ad} < H$ for functions of $\vec{r}$ and $\vec{R}$ which, for fixed $\vec{R}$, are quadratically integrable in $\vec{r}$, a property of $P\Psi_B$. The second inequality is an assumption.

Choosing H_t to be given not by Eq. (2.14) but by

$$H_t - E_{T0} = P(H_{ad} - E_{T0})P , \tag{2.31a}$$

and noting that $\Psi_{ad}(\vec{r}, \vec{R})$ defined by Eqs. (2.17)–(2.20) satisfies

$$P(H_{ad} - E_{T0})P\Psi_{ad} = 0 \tag{2.31b}$$

and the necessary boundary conditions, (2.11) becomes

$$\begin{aligned} A_{ad} = A &+ (\Psi, P[H_{ad} - E_{T0}]P\Psi) \\ &-(\delta\Psi, P[H_{ad} - E_{T0}]P\delta\Psi) . \end{aligned} \tag{2.32}$$

[The choice (2.14) for H_t also gives (2.32) after a cancellation of terms involving $Q\Psi$, where $Q = 1 - P$.] Since $H_{ad} - E_{T0}$ can support one and only one bound state in $\vec{R}$ space, with eigenfunction and eigenvalue to be denoted by $u_{B,ad}(R)$ and $E_{B,ad}$, respectively, it follows that $P[H_{ad} - E_{T0}]P$ can support one and only one bound state in $\vec{R}$ and $\vec{r}$ space (with eigenvalue $E_{B,ad}$ and eigenfunction $\psi_{T0}u_{B,ad}$). It follows[2] from (2.30a) that $P\Psi_B$ is good enough to effectively "extract" the effect of the bound state of $P(H_{ad} - E_{T0})P$ and to enable us to construct the positive definite operator

$$P(H_{ad} - E_{T0}) - \frac{(H_{ad} - E_{T0})P\,\Psi_B)(P\Psi_B(H_{ad} - E_{T0})}{(P\Psi_B, (H_{ad} - E_{T0})P\Psi_B)} \geqslant 0. \tag{2.33}$$

In arriving at this last result, we used the fact that since P operates in $\vec{r}$ space and therefore commutes with $H_{ad} - E_{T0}$, we have

$$P(H_{ad} - E_{T0}) = P(H_{ad} - E_{T0})P = (H_{ad} - E_{T0})P.$$

We now insert (2.33) into the last term of (2.32); note that the presence of the decaying function $P\Psi_B$ enables us to transfer when necessary $H_{ad} - E_{T0}$ so that it operates on $\delta\Psi$. We use

$$(H_{ad} - E_{T0})\delta\Psi = -(H_{ad} - E_{T0})\Psi = (H - H_{ad})\Psi ,$$

a consequence of (2.22), (2.17), and (2.4).

We also use the relationship

$$\begin{aligned} P(H_{ad} - E_{T0})\Psi &= -(H - H_{ad})\Psi + Q(E_{T0} - H_{ad})\Psi \\ &= -(H - H_{ad})\Psi + Q(E_{T0} - H_{ad})Q\Psi \end{aligned}$$

in the second term of (2.32).

We then arrive at

$$A_{ad}-A \leqslant -(\Psi, J\Psi)+(Q\Psi, (E_{T0}-H_{ad})Q\Psi)\ ,$$

where

$$J=(H-H_{ad})-\frac{(H-H_{ad})P\Psi_B\rangle\langle P\Psi_B(H-H_{ad})}{(P\Psi_B, (E_{T0}-H_{ad})P\Psi_B)}\ .$$

As a consequence of (2.30a) we have

$$J>J'\equiv(H-H_{ad})-\frac{(H-H_{ad})P\Psi_B\rangle\langle P\Psi_B(H-H_{ad})}{(P\Psi_B,(H-H_{ad})P\Psi_B)}\ . \tag{2.34}$$

Since $H-H_{ad}\geqslant 0$ for fixed $\vec{\mathrm{R}}$ and for functions quadratically integrable in $\vec{\mathrm{r}}$, as Ψ is, the Schwarz inequality gives $(\Psi, J'\Psi)\geqslant 0$. Furthermore, since $H-E_{T0}$ has only one bound state, there cannot be two normalizable orthogonal functions each of which generates a negative expectation value of $H-E_{T0}$; we will use this result in a moment.

Finally, by assuming the inequality

$$(Q\Psi, (H_{ad}-E_{T0})Q\Psi)\geqslant 0\ , \tag{2.30b}$$

we obtain the desired result, namely,

$$A_{ad}\leqslant A\ . \tag{2.35}$$

It follows from (2.30a) that $Q(H-E_{T0})Q>0$, and thus (2.30b) is expected to be valid when the effect of $Q(H_T+V-\mathcal{E}_0)Q$ is small.

The result (2.35) can be generalized; by assuming the generalization of the second inequality in (2.30a), one can show that $A_{ad}\leqslant A$ if H and H_{ad} support the same number of bound states. Apart from the need for the assumed inequality, the result is analogous to the inequality relating A and A_{stat} quoted above.[3] Further, the result is not unexpected from the physical picture; this should be clearer after the discussion of Sec. II C. We suspect that the assumed inequality, the second inequality in (2.30a), is not necessary for the proof of (2.35), but we have been unable to prove (2.35) without having assumed the inequality.

C. H_{ad} can support more bound states than H can

If H cannot support as many bound states as H_{ad} can, the inequality $A_{ad}\leqslant A$ need not be true. The situation is very similar to that which obtains in elastic scattering at nonzero incident energies. There, for potential scattering, one knows from the monotonicity theorem that $V_2(r)\geqslant V_1(r)$ implies that $\eta_2\leqslant\eta_1$, where η_i is the phase shift for some given angular momentum associated with $V_i(r)$; with appropriate definitions of η, the result can often be extended to scattering by compound systems. However, $V_2(r)\geqslant V_1(r)$ does *not* necessarily imply that $\tan\eta_2\leqslant\tan\eta_1$; this latter relationship will be true if $\tan\eta_2/k^{2L+1}$ and $\tan\eta_1/k^{2L+1}$ have passed through infinity the same number of times. Correspondingly, since

$$A\equiv-\lim_{k\to 0}\,(\tan\eta_L/k^{2L+1}), \tag{2.36}$$

$V_2(r)\geqslant V_1(r)$ does not necessarily imply that $A_2\geqslant A_1$. $V_2(r)\geqslant V_1(r)$ will imply $A_2\geqslant A_1$ if A_1 and A_2 have passed through infinity the same number of times.

D. Bound on the "scattering-length phase"

Just as we have a monotonicity theorem for η but not for $\tan\eta$, so we have a monotonicity theorem for γ but not for A, where γ is the "scattering-length phase" defined[13] by

$$A=-\tan\gamma\ . \tag{2.37}$$

Whereas $A(\lambda)$ can pass discontinuously from $+\infty$ to $-\infty$ or from $-\infty$ to $+\infty$, $\gamma(\lambda)$ can be defined to be a continuous function of the strength λ of the potential λV. γ therefore plays a role for $k=0$ very similar to the role played by η for $k>0$. Since $H_{ad}\leqslant H$, we have

$$\gamma_{ad}\geqslant\gamma, \tag{2.38}$$

where γ_{ad} is defined by

$$A_{ad}=-\tan\gamma_{ad}\ . \tag{2.39}$$

Equation (2.38) is valid whether or not H and H_{ad} support the same number of bound states. Of course, (2.38) is less meaningful than (2.27) or (2.35) or their generalization if H and H_{ad} support the same number of bound states and if Eqs. (2.30) are valid, since the cross section is related to $\sin^2\eta$ and not directly to η.

III. FURTHER STUDY OF ADIABATIC PICTURE: EQUIVALENT ADIABATIC HAMILTONIAN

As indicated earlier, the choice $H_t=H_{ad}$ as given by Eq. (2.14) is not the only choice that provides a mathematical framework within which adiabaticlike approximations can be studied. To obtain other such Hamiltonians, we begin by recording the identity

$$H-E_{T0}=P(T+\mathcal{E}_0-E_{T0})P+Q(T+\mathcal{E}_0-E_{T0})Q+(H_T+V-\mathcal{E}_0)\ . \tag{3.1}$$

The validity of Eq. (3.1) follows immediately on noting that both $P=\psi_{T0}\rangle\langle\psi_{T0}$ and $Q=1-P$ commute with $T+\mathcal{E}_0-E_{T0}$. The first term in (3.1) must surely be retained in any H_t-E_{T0} which is to be used to study adiabaticlike approximations; it represents the scattering of a particle by the adiabatic potential $\mathfrak{V}_0(R)$. This suggests three possibilities as our choice for H_t-E_{T0}, the first and second terms of (3.1), the first term alone, or the first and third terms. Since $\mathcal{E}_0 - E_{T0} = \mathcal{V}_0$, our three choices are therefore

$$H_t - E_{T0} = T + \mathcal{V}_0 \equiv H_{ad}^{(1)} - E_{T0}, \tag{3.2}$$

$$H_t - E_{T0} = P(T + \mathcal{V}_0)P \equiv H_{ad}^{(2)} - E_{T0}, \tag{3.3}$$

and

$$H_t - E_{T0} = P(T + \mathcal{V}_0)P + (H_T + V - \mathcal{E}_0) \equiv H_{ad}^{(3)} - E_{T0}. \tag{3.4}$$

$H_{ad}^{(1)}$ is of course just the H_{ad} of Sec. II. (The first two of the above choices for H_t were used in Sec. II.) From the above definitions and from (3.1), it follows immediately that

$$H - H_{ad}^{(1)} = H_T + V - \mathcal{E}_0,$$

$$H - H_{ad}^{(2)} = Q(T + \mathcal{V}_0)Q + H_T + V - \mathcal{E}_0,$$

$$H - H_{ad}^{(3)} = Q(T + \mathcal{V}_0)Q.$$

We will assume throughout this section that $\mathcal{V}_0$ cannot support a bound state, that is, that $T + \mathcal{V}_0$ is non-negative with respect to quadratically integrable functions. [The generalization to the case where the true and adiabaticlike Hamiltonians support the same number of bound states and where Eqs. (2.30) are valid would proceed as in Sec. II.] Since $Q\Psi$ is quadratically integrable, it follows that

$$(Q\Psi, (T + \mathcal{V}_0)Q\Psi) \geq 0.$$

Since $H_T + V - \mathcal{E}_0$ is non-negative, a derivation identical in form to that used in arriving at (2.24) leads to

$$A_{ad}^{(p)} \leq A - (\delta\Psi^{(p)}, (H_{ad}^{(p)} - E_{T0})\delta\Psi^{(p)}) \tag{3.5}$$

for $p = 1$, 2, or 3; we have $\delta\Psi^{(p)} = \Psi_{ad}^{(p)} - \Psi$, where $\Psi_{ad}^{(p)}$ is defined by $(H_{ad}^{(p)} - E_{T0})\Psi_{ad}^{(p)} = 0$ and by the usual boundary conditions. $A_{ad}^{(p)}$ appears in the asymptotic form of $\Psi_{ad}^{(p)}$.

Since $\delta\Psi^{(p)}$ is also quadratically integrable, Eq. (3.5) reduces immediately to

$$A_{ad}^{(p)} \leq A, \tag{3.6}$$

a result of the desired form. The three bounds provided by Eq. (3.6) are in reality only one bound, which is written

$$A_{ad} \leq A. \tag{3.7}$$

To see that

$$A_{ad}^{(2)} = A_{ad}^{(1)} \equiv A_{ad}, \tag{3.8}$$

note that $H_{ad}^{(2)}$ and $H_{ad}^{(1)}$ differ only in the Q term of (3.1), and effects of the Q term play no role in the determination of $A_{ad}^{(1)}$ because of the boundary conditions (2.5) and (2.18); this constitutes the proof of Eq. (3.8). To see that

$$A_{ad}^{(3)} = A_{ad}^{(1)}$$

is a little more difficult. We have

$$(H_{ad}^{(3)} - E_{T0})\Psi_{ad}^{(3)} = 0. \tag{3.9}$$

$H_{ad}^{(3)}$, defined by Eq. (3.4), is a rather complicated operator, and it would be extremely difficult to obtain $\Psi_{ad}^{(3)}$. In fact, however, we do not need to know $\Psi_{ad}^{(3)}$ to evaluate $A_{ad}^{(3)}$; we need only know $P\Psi_{ad}^{(3)}$. But using the results of Appendix A, we can immediately convert (3.9) into

$$P(T + \mathcal{V}_0)P\Psi_{ad}^{(3)} = 0.$$

Since $P\Psi_{ad}^{(3)}$ and $P\Psi_{ad}^{(1)}$ satisfy the same equation and the same boundary condition, we have $P\Psi_{ad}^{(3)} = P\Psi_{ad}^{(1)}$ and therefore $A_{ad}^{(3)} = A_{ad}^{(1)}$.

We comment now on the relative merits of the different forms of approximate Hamiltonians. Equation (3.2) is the simplest form, but there are some ambiguities in its use. In particular, the boundary condition (2.18) seems somewhat forced. In (3.3), on the other hand, the boundary condition (2.18) is built into the operator, and solutions of the form

$$\psi_n(\vec{r})u_{ad}(R), \quad n \neq 0 \tag{3.10}$$

involving the same function u_{ad} that appears in (2.19), are not allowed. Furthermore, as opposed to the use of (3.2), the use of (3.3), because of the elimination of terms of the form given by (3.10), enables us to derive a monotonicity theorem on the scattering-length phase γ of (2.35). Thus, let $\Psi(\lambda)$ be defined as the solution for $0 \leq \lambda \leq 1$ of

$$[H(\lambda) - E_{T0}]\Psi(\lambda) \equiv [H_{ad}^{(2)} + \lambda(H - H_{ad}^{(2)}) - E_{T0}]\Psi(\lambda) = 0,$$

$$\Psi(\lambda) \to (M_{\text{red}}/2\pi\hbar^2)^{1/2}\psi_0(\vec{r})[R^L - A(\lambda)/R^{L+1}], \quad R \to \infty.$$

With $\Psi(\lambda)$ the trial function in a study of the determination of $A(\lambda + d\lambda)$, we obtain the identity

$$\begin{aligned} A(\lambda + d\lambda) = A(\lambda) \\ &+ \int \Psi(\lambda + d\lambda)[H(\lambda + d\lambda) - E_{T0}]\Psi(\lambda)\, d\vec{r}\, d\vec{R}, \\ &= A(\lambda) + d\lambda \int \Psi(\lambda + d\lambda)(H - H_{ad}^{(2)})\Psi(\lambda) d\vec{r}\, d\vec{R}. \end{aligned}$$

With

$$A(\lambda) = -\tan\gamma(\lambda),$$

this becomes

$$\frac{\partial\gamma(\lambda)}{\partial\lambda} = -\cos^2\gamma(\lambda) \int \Psi(\lambda)(H - H_{ad}^{(2)})\Psi(\lambda)\, d\vec{r}\, d\vec{R} \leq 0.$$

It follows that $\gamma(0) \geq \gamma(1)$, that is, that

$$\gamma_{ad} \geq \gamma.$$

Much more significant is the probability that the use of (3.3) will enable us to extend the approach to obtain bounds on scattering parameters in the positive energy region, that is, for $E > E_{T0}$. (Note that the identity (3.1) remains valid with E_{T0} replaced by E throughout.)

The primary interest of $H_{ad}^{(3)}$ is the fact that it seems to be the best starting point from the physical point of view for the determination of bounds; the neglect of $Q(T+\mathcal{V}_0)Q$ is perhaps the most natural mathematical formulation of the adiabatic approximation.

$H_{ad}^{(1)}$ and $H_{ad}^{(2)}$ have the very great advantage over $H_{ad}^{(3)}$, for $E > E_{T0}$, that they are the usual adiabatic approximation. Any theorems deduced from $H_{ad}^{(1)}$ and $H_{ad}^{(2)}$ give additional significance to the numerical results obtained in the usual adiabatic calculations. The use of $H_{ad}^{(3)}$ for $E > E_{T0}$ would require a more difficult calculation.

Bounds on the binding energy E_B of the system can be obtained using any of the operators $H_{ad}^{(p)}$, as was done earlier[14,15] using $H_{ad}^{(1)}$. We will elaborate further on this point in a later publication in connection with a variational determination of lower bounds on E_B.

IV. ANGULAR-MOMENTUM COUPLING

The formal discussion of bounds on scattering lengths presented in Secs. II and III does not explicitly analyze the coupling of the angular momenta of the target and projectile. The kinematics associated with the angular momentum coupling can be useful for applications, however, and we briefly consider here several ways of formulating this part of the problem, which may at times give rise to slightly different bounds. The laboratory frame will be denoted by $\mathcal{S}$ and the variables in that frame will not be primed. The body-fixed frame will be denoted by $\mathcal{S}'$ and the variables in that frame will be primed. $\hat{R}$ defines the z' axis of $\mathcal{S}'$, that is, we have $\hat{z}'=\hat{R}$; R is measured in the frame $\mathcal{S}$.

While most of the following considerations can almost surely be extended to targets with many particles, it will greatly simplify the discussion if we restrict ourselves to targets, such as hydrogen atoms, containing only two particles. The total Hamiltonian H can then be written

$$H = t_R + t_r + \frac{1}{2m_{\text{red}}\,r^2}\vec{1}^2 + \frac{1}{2M_{\text{red}}R^2}\vec{j}^2 + W(r,R,\alpha), \tag{4.1}$$

where t_R is the radial part of the kinetic-energy operator for the relative motion of the projectile and the center of mass of the target, with a reduced mass M_{red}; t_r is the radial part of the internal-kinetic-energy operator for the target system with a reduced mass m_{red}; $\vec{1}^2$ is the square of the target internal angular momentum operator in the frame $\mathcal{S}$; $\vec{j}^2$ is the square of the angular momentum operator for the relative motion of the projectile and the target center of mass in the frame $\mathcal{S}$; and $W(r,R,\alpha)=V(\vec{r},\vec{R})+U_T(\vec{r})$, where $U_T(\vec{r})$ is the interaction between the target particles, and α denotes the angle between $\hat{r}$ and $\hat{R}$. Since the square of the total angular momentum operator $\vec{L}^2$ of the system given by

$$\vec{L}^2 = (\vec{1}+\vec{j})^2, \tag{4.2}$$

and the projection of $\vec{L}$ onto the $\hat{z}$ axis in the frame $\mathcal{S}$, L_Z, are conserved, it will be useful to introduce the set of eigenfunctions

$$\mathcal{Y}_{lj}^{LM}(r,R) = \sum_{m_l m_j} (lj\,m_l m_j \,|\, LM) Y_{l m_l}(\hat{r}) Y_{j m_j}(\hat{R}) \tag{4.3}$$

of $\vec{L}^2$ and L_z. The total wave function Ψ can be expanded in terms of the $\mathcal{Y}$'s as

$$\Psi^{LM}(\vec{r},\vec{R}) = \sum_{lj} f_{lj}^{L}(r,R)\mathcal{Y}_{lj}^{LM}(\hat{r},\hat{R}), \tag{4.4}$$

where $\vec{1}^2$ and $\vec{j}^2$ are in general not conserved because of the interaction $V(\vec{r},\vec{R})$ which explicitly depends on the angle α. Note that all the angles which appear in (4.3) and (4.4) are measured in the frame $\mathcal{S}$.

Evidently, the choice of variables in (4.3) is not unique; most of the different choices are related to one another by appropriate rotations. One choice[16] is to take, in addition to r and R, the angle α between $\hat{r}$ and $\hat{R}$, the polar angles of $\hat{R}$ in $\mathcal{S}$, that is, Θ and Φ, and the angle Ω between the planes defined by $(\hat{r},\hat{R})$ and $(\hat{R},\hat{z})$. The new set is

$$(\vec{r}',\vec{R}) \equiv (r,\alpha;R,\Theta,\Phi,\Omega), \tag{4.5}$$

whereas the set used in (4.3) and (4.4) was

$$(\vec{r},\vec{R}) = (r,\theta,\phi;R,\Theta,\Phi). \tag{4.6}$$

The introduction of the variable α in (4.5) might be convenient since the potential V depends only on this angle and the radial variables r and R. However, except for $L=0$, the variables (r,R,α) and the Euler angles (Θ,Φ,Ω) do not separate in the kinetic energy terms of (4.1) that contain $\vec{1}^2$ and $\vec{j}^2$, as there occurs a coupling term of the form $\partial^2/\partial\Omega\partial\alpha$.[16,17] The total wave function Ψ in the set (4.5), e.g., may then be expanded in terms of the rotation matrices, the $\mathcal{D}$'s, as

$$\Psi^{LM}(\vec{r}',\vec{R}) = \sum_K f_L{}^K(r,R,\alpha)\mathcal{D}_{MK}^{L}(\Theta,\Phi,\Omega), \tag{4.8}$$

where K is the quantum number associated with the projection of the total angular momentum $\vec{L}$ onto the body-fixed z' axis, that is, onto $\hat{R}$. Presumably, the form (4.8) would be more useful in the case of ion-atom collisions at low energies, where the Born-Oppenheimer picture, for which K is often a good quantum number, is more appropriate. In fact, in the usual molecular state calculations with the vector $\vec{R}$ fixed, the variable $\vec{r}'$ in the frame $\mathcal{S}'$ is used to evaluate the electronic wave functions and its adiabatic energies.

After these preliminary discussions, we now return to the problem of bounds. Dropping the t_R term in (4.1) and recalling the form (4.4), we can immediately project the problem onto a subspace of given L and M, and consider the adiabatic problem defined by

$$\left(t_r+\frac{1}{2m_{\mathrm{red}}r^2}\vec{l}^2+\frac{1}{2M_{\mathrm{red}}R^2}\vec{j}^2+W(r,R,\alpha)\right)\phi_n^{LM}(\vec{r};\vec{R}) = \mathcal{E}_n^L(R)\phi_n^{LM}(\vec{r};\vec{R}) . \quad (4.9)$$

(We could also take the projection of the operator in large parentheses onto the subspace of given L and M, but it is not necessary to do so.) To actually determine $\mathcal{E}_n^L(R)$, ϕ_n^{LM} would be expanded in terms of $\mathcal{Y}$'s just as in (4.4); (4.9) then gives rise to an infinite set of coupled equations in the variable r for different allowed sets of (l,j). These coupled equations have been found to be tractable for the scattering of an electron by a hydrogen molecule,[18] and should be tractable for a number of other problems. The inequality (2.16b) is replaced by

$$H_L \geq t_R+\mathcal{E}_0^L(R)\equiv\tilde{H}_{L,\mathrm{ad}} , \quad (4.10)$$

where $\mathcal{E}_0^L(R)$ is the lowest-energy eigenvalue for the given L and R. The solution of (2.17), with H_{ad} replaced by $\tilde{H}_{L,\mathrm{ad}}$ of (4.10), and the boundary conditions (2.18), gives a bound

$$A_L \geq \tilde{A}_{L,\mathrm{ad}} , \quad (4.11)$$

provided of course that the number of bound states supported by H_L and by $\tilde{H}_{L,\mathrm{ad}}$ is the same, as discussed in Sec. II. The bound (4.11) obtained from (4.10) is rigorous and in principle applicable to all values of L. However, many of the molecular wave functions and energy calculations which are available do not employ the form (4.9), but rather the form involving $\vec{r}'$ in the frame $\mathcal{S}'$. Thus it is also of interest to consider the adiabatic problem defined by

$$\left(t_r+\frac{1}{2m_{\mathrm{red}}r^2}\vec{l}'^2+W(r,R,\alpha)\right)\phi_n'(\vec{r}';\vec{R}) = \mathcal{E}_n(R)\phi_n'(\vec{r}';\vec{R}) , \quad (4.12)$$

where $\vec{l}'^2$ is the square of the target internal angular momentum operator in the frame $\mathcal{S}'$. The analogous equation in the frame $\mathcal{S}$ is

$$\left(t_r+\frac{1}{2m_{\mathrm{red}}r^2}\vec{l}^2+W(r,R,\alpha)\right)\phi_n(\vec{r};\vec{R}) = \mathcal{E}_n(R)\phi_n(\vec{r};\vec{R}) . \quad (4.13)$$

As indicated by the notation, the energies for the two equations are the same; the wave functions are related by a rotation, that is,

$$\phi_n(\vec{r};\vec{R})=\mathcal{R}(\Theta,\Phi,\Omega)\phi_n'(\vec{r}';\vec{R}) , \quad (4.14)$$

where $\mathcal{R}$ is the rotation operator connecting the frames $\mathcal{S}$ and $\mathcal{S}'$.

Using Eq. (4.13), the inequality (2.16b) is now replaced by

$$H_L \geq t_R+\frac{\hbar^2}{2M_{\mathrm{red}}R^2}L(L+1)+\mathcal{E}_0(R)\equiv H_{L,\mathrm{ad}} , \quad (4.15)$$

where $\vec{j}^2$ has been replaced by $L(L+1)\hbar^2$. (As always throughout this paper, we are assuming that the target ground state has zero angular momentum.) Again the solution of (2.17), with H_{ad} replaced by $H_{L,\mathrm{ad}}$ of (4.15), and the boundary conditions (2.18), gives

$$A_L \geq A_{L,\mathrm{ad}} , \quad (4.16)$$

provided H_L and $H_{L,\mathrm{ad}}$ both support exactly the same number of bound states.

Evidently, two slightly different angular momentum decompositions of (2.16b) gave rise to two different bounds, (4.11) and (4.16). In general it is difficult to determine in advance which of the two approaches will give the better bound. However, we have, comparing (4.9) and (4.13) and noting that $\vec{j}^2$ is a positive operator,

$$\mathcal{E}_n^L \geq \mathcal{E}_n , \quad (4.17)$$

and thus, choosing $L=0$ and comparing (4.10) and (4.15),

$$A_{L=0} \geq \tilde{A}_{L=0,\mathrm{ad}} \geq A_{L=0,\mathrm{ad}} , \quad (4.18)$$

under the same conditions stated earlier for the validity of (4.11) and (4.16).

The inequality (4.16) is especially useful in practice, for the simple reason that $\mathcal{E}_n(R)$ of (4.12) and (4.13) are readily available for many complex molecular systems when appropriate reduced-mass corrections are incorporated in the form of scaling parameters for the energies and length units. On the other hand, $\tilde{A}_{L,\mathrm{ad}}$ requires a new calculation using (4.9) which is more difficult than (4.12). But, at least for $L=0$, the resulting bound would be an improvement over the result obtained from (4.12) and (4.13).

As is clear from (4.9) and (4.13), the angular momentum projections on to a state of definite L and M at different stages of the calculations yield different scattering length bounds. Thus, when the vector $\vec{R}$ is held fixed during the $\mathcal{E}_0$ calculation, we cease to have a system with a well defined total angular momentum. (Localization at a point requires a superposition of all possible angular momenta.) However, the L dependence of A_L is recovered in (4.15), so that the bound thus obtained is still rigorously valid. In contrast, when the scalar R is fixed, as in (4.9) with the angular variations in $\hat{R}$ already incorporated in the calculation of ϕ^{LM}, the quantum numbers L and M are constant throughout the calculation.

V. APPLICATIONS

In this section, we consider several applications of the bounds on A developed in Secs. II and IV. Specifically, we discuss the e^+H, e^+He, and pH systems, for each of which $\mathcal{V}_0$ is known, and a constructed two-channel model which can be studied in depth by varying the parameters contained in the model. The role of symmetry with regard to pH scattering is discussed in Appendix B; the analysis in this section assumes that the two protons are in a spatially symmetric state.

A. e^+H scattering

The scattering length for positron-hydrogen atom scattering was obtained to very high precision by a variational calculation which yielded[19] (retaining only two significant figures)

$$A(L=0) = -2.1a_0, \tag{5.1}$$

where a_0 is the Bohr radius. Since e^+ and e^- have the same mass, there is no reason to assume that the adiabatic approximation in which we first fix the positron will yield good results, but the bound (2.27) should still be valid under the appropriate conditions. In fact, since the true e^+H system has no bound states, while the e^+H system in the adiabatic approximation *does* have a bound state, (2.27) need not be correct. Indeed, with the $\mathcal{V}_0$ of Bates and Reid,[20] the numerical solution of (2.20) for zero total angular momentum ($L=0$) yields $A_{ad} \approx 19a_0$, which obviously violates the bound (2.27). We have neglected here small corrections of order m_e/M_p connected with the scaling of energies and lengths, which are necessary in general to convert the adiabatic energies calculated in the scaled units.[20,21] We can however use the Hamiltonian $H(L=0)$ of Eq. (2.16b), obtained by projecting H onto the space of total orbital angular momentum zero. The associated adiabatic potential $\mathcal{V}_0(L=0)$ *cannot*[15] support a bound state of e^+ +H, and the use of $\mathcal{V}_0(L=0)$ must yield a bound on A. The use of $\mathcal{V}_0(L=0)$ in (2.20) yields

$$A_{ad}(L=0) = -24a_0 < A\ .$$

We do find a legitimate, if very poor, bound.

From the fact that $\mathcal{V}_0(L=0)$ cannot support a bound state, and from the relationship $H_{ad} < H$, we conclude that a true bound state of the e^+H system does not exist, in agreement with a previous finding.[15]

B. e^+He scattering

The positron-helium adiabatic potential has been studied extensively.[22] Stuart and Matsen give the potential $\mathcal{V}_0(R)$ over the range for which it is negative, from $1a_0$ on out. A_{ad} is relatively insensitive to precisely how the potential is extrapolated toward the origin. [$\mathcal{V}_0(R)$ should clearly approach $(2e^2/R)$ plus the difference in binding energies of Li$^+$ and He.] Using such an extrapolation, we find that $\mathcal{V}_0$ cannot support a bound state and that

$$A_{ad}(L=0) \approx (-0.7 \pm 0.1)a_0;$$

this probably represents a lower bound within the estimated error.

The true value of A cannot readily be estimated theoretically because of the complexity of (and uncertainty in) the helium ground-state wave function. Many estimates are available,[23] all of which point to an approximate value

$$A \approx (-0.5 \pm 0.1)a_0 > A_{ad}\ .$$

The bound is therefore satisfied. In view of the fact that we are here too fixing the light positron, the result is suspiciously good.

C. pH scattering

If we think of m_e/M_p as arbitrarily small, the adiabatic approximation, in which we fix the proton-proton separation and allow the very light electron to run around, is exact; the question of obtaining bounds on the scattering length (or binding energy) does not then arise. If on the other hand, we are interested in corrections of order m_e/M_p, or some power thereof, the adiabatic approximation is not exact and the determination of bounds is of interest. The adiabatic potential in the latter problem, in which we fix the separation of the incident proton and the center of mass of the hydrogen atom, is obtained from the adiabatic approximation with the proton-proton separation fixed by scaling.[14] An adiabatic calculation of the vibrational levels of the lowest electronic state of the H_2^+ system can be expected physically, as noted above, to be very accurate; more concretely, Wind[24] has shown that the nonadiabatic corrections are quite small. It is then reasonable to assume that the number of vibrational bound states of the lowest electronic level in the adiabatic approximation is the same as the true number. (The adiabatic approximation gives 19, 18, and 17 vibrational bound states for the rotational quantum number $j=0$, 2, and 4, respectively.) Our considerations are restricted to the scattering length associated with $j=0$ scattering. The cases with $j>0$ can be treated analogously, but the problem of the determination of bounds is of an entirely different character, because the adiabatic potential $\mathcal{V}_0$ behaves at large values of R as $-\alpha_0/R^4$, where α_0 is the dipole polarizability of the hydrogen atom. The leading behavior of $\tan\eta_L(L=j)$ is therefore given by[25]

$$\tan\eta_L=\pi\alpha_0 k^2[(2L+3)(2L+1)(2L-1)a_0]^{-1},$$

and the determination of bounds on $\tan\eta_L$ reduces to the determination of bounds on α_0.

We return now to the $L=0$ case. The effective potential $\mathcal{V}_0$ can now be used, in conjunction with (2.20), to obtain A_{ad}. (Note that the zero-energy adiabatic scattering wave function u_{ad} has 19 nodes.) It is very much simpler, though it entails a loss of accuracy, to use effective range theory and the binding energy in the adiabatic approximation of the state which is least bound, the $v=19$, $j=L=0$ level, with an energy

$$E_{ad}(v=19, L=0)=-(\hbar^2/2M_{\text{red}})\kappa^2{}_{19,ad}$$
$$\approx -4.4\times 10^{-6}\text{ a.u.},$$

obtained from Fig. 2 of Wind. Lengths are in units of $a_0=\hbar^2/m_e e^2$, where m_e is the electron mass, and energies are in units of $e^2/2a_0$. The reduced mass is one-half the proton mass. If we neglect the term with the effective range, and apply effective range theory within the framework of the adiabatic approximation, we obtain

$$A_{ad}\approx(\kappa_{19,ad})^{-1}\approx 7.9a_0.$$

If one includes the leading nonadiabatic correction term, one obtains the improved estimate[24]

$$E(v=19, L=0)\approx -3.98\times 10^{-6}\text{ a.u.}$$

Effective range theory now gives

$$A\approx 8.3a_0.$$

Clearly, once one has the corrected energy estimate, the adiabatic approximation serves no purpose. We have included an estimate of A_{ad}—even though, as noted above, A_{ad} does not provide a bound even apart from the approximation involved in using effective-range theory—to obtain some idea of the accuracy that can be achieved in the adiabatic approximation.

D. Two-channel model

In order to study the accuracy of the bound derived in Sec. II, and further, to confirm that the bound is indeed valid when H and H_{ad} have the same number of bound states, we construct a simple two-state model and study A and A_{ad} as functions of the parameters contained in the model. With the Hamiltonian given by (2.1), and with the target assumed to have only two states, with energies and normalized wave functions E_{T1} and $\psi_{T1}(\vec{r})$, and E_{T2} and $\psi_{T2}(\vec{r})$, respectively, we write

$$\Psi(\vec{r},\vec{R})=\psi_{T1}(\vec{r})u_1(\vec{R})+\psi_{T2}(\vec{r})u_2(\vec{R}). \tag{5.1a}$$

Substitution of (5.1a) into the zero-incident-kinetic-energy scattering equation gives a set of two coupled equations

$$\begin{aligned}\left(-\frac{\hbar^2}{2m}\frac{d^2}{dR^2}+V_{11}\right)u_1&=-V_{12}u_2,\\ \left(-\frac{\hbar^2}{2m}\frac{d^2}{dR^2}+V_{22}+E_{T2}-E_{T1}\right)u_2&=-V_{21}u_1,\end{aligned} \tag{5.1b}$$

where m is the reduced mass and where

$$V_{nm}\equiv\int d\vec{r}\,\psi^*_{Tn}V\psi_{Tm};$$

we assume all relevant angular momenta to have the value zero. Since ψ_{T1} and ψ_{T2} form a complete set in the present model, the adiabatic approximation wave functions $\phi_n(\vec{r};\vec{R})$ can be expressed as

$$\begin{aligned}\phi_1(\vec{r};\vec{R})&=\psi_{T1}(\vec{r})\omega_1(\vec{R})+\psi_{T2}(\vec{r})\omega_2(\vec{R}),\\ \phi_2(\vec{r};\vec{R})&=-\psi_{T1}(\vec{r})\omega_2(\vec{R})+\psi_{T2}(\vec{r})\omega_1(\vec{R}),\end{aligned} \tag{5.2}$$

where the coefficient functions ω_1 and ω_2 must have values such that the normalization and orthogonality conditions are satisfied, that is, such that

$$\int\phi^*_n\phi_m\,d\vec{r}=\delta_{nm}\quad\text{for each fixed }\vec{R}.$$

We therefore have

$$\omega_1^2+\omega_2^2=1.$$

ϕ_n satisfies (2.12), with $\mathcal{E}_n=E_{Tn}+\mathcal{V}_n$. Inserting each of Eqs. (5.2) in turn into (2.12), and projecting onto $\psi_{Tn}(\vec{r})$, we have

$$\begin{aligned}(E_{T1}+V_{11}-\mathcal{E}_1)\omega_1&=-V_{12}\omega_2,\\ (E_{T2}+V_{22}-\mathcal{E}_1)\omega_2&=-V_{21}\omega_1\end{aligned}$$

and

$$\begin{aligned}(E_{T1}+V_{11}-\mathcal{E}_2)\omega_2&=+V_{12}\omega_1,\\ (E_{T2}+V_{22}-\mathcal{E}_2)\omega_1&=+V_{21}\omega_2.\end{aligned}$$

Rather than parametrizing the model by specifying V_{nm} and E_{Tn}, it will be convenient to choose the values for $\mathcal{V}_1, \mathcal{V}_2, \omega_1, \omega_2, E_{T1}$, and E_{T2}; these completely determine the model. Explicitly, we set

$$\omega_1 = \sin\rho, \quad \omega_2 = \cos\rho \quad \text{for } R < R_0$$

and

$$\omega_1 = 1, \quad \omega_2 = 0 \qquad \text{for } R \geqslant R_0,$$

where

$$\rho = (\pi R/2R_0);$$

in addition, we choose $R_0 = 2a_0$, $E_{T1} = -2$ Ry, $E_{T2} = -1$ Ry, and

$$\mathcal{V}_1 = -\mathcal{V}_2 = -G\cos\rho \quad \text{for } R < R_0,$$

$$\mathcal{V}_1 = \mathcal{V}_2 = 0 \qquad \text{for } R \geqslant R_0.$$

The coupling constant G (in Ry) is varied in the calculation. The V_{nm}'s are given then, for $R \leqslant R_0$, by

$$V_{11} = \cos^2\rho + G\cos\rho\cos(2\rho) = -V_{22},$$

$$V_{12} = -\sin\rho\cos\rho(E_{T2} - E_{T1} + 2G\cos\rho) = V_{21},$$

and

$$V_{nm} = 0 \quad \text{for } R \geqslant R_0.$$

The $L = 0$ scattering lengths are calculated for the static and adiabatic approximations from the equations

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dR^2} + V_{11}\right)u_{\text{stat}} = 0,$$

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dR^2} + \mathcal{V}_1\right)u_{ad} = 0,$$

and the usual boundary conditions. The approximate values, A_{stat} and A_{ad}, are compared with the exact value A obtained from the numerical solution of the coupled equations (5.1b). The results are summarized in Table II. As expected, the inequality $A > A_{ad}$ is violated only for values of G for which the number of composite bound states in the adiabatic approximation, N_{ad}, differs from the true number, N. Note however that when H and H_{ad} can each support one bound state, we must also consider the second inequality in (2.30a), and (2.30b). Writing

$$P\Psi_B = \psi_{T1}(\vec{r})u_B(\vec{R}),$$

where

$$u_B(\vec{R}) = \int d\vec{r}\,\psi_{T1}(\vec{r})\psi_B(\vec{r},\vec{R}),$$

the second inequality in (2.30a) can be written

$$\int d\vec{R}\,u_B(\vec{R})[T(R) + V_{11}(R)]u_B(\vec{R}) < 0. \tag{5.3}$$

(The ground state in our model is labeled 1 rather than zero.) A necessary (but not sufficient) condition for the validity of (5.3) is that there be a bound state in the static approximation. In summary, then, for the first five entries in Table II, we have $N_{\text{stat}} = N = N_{ad} = 0$, and we can predict that $A_{\text{stat}} \geqslant A \geqslant A_{ad}$; these inequalities can indeed be seen to be satisfied. For the next 3 entries, we have $N_{\text{stat}} = N \neq N_{ad}$, and all that we can be certain of is that $A_{\text{stat}} > A$; we can not guarantee any inequalities involving A_{ad}. For the last 4 entries, we have $N_{\text{stat}} \neq N = N_{ad} = 0$, and (5.3) is not satisfied. We cannot therefore guarantee any scattering length inequalities. Nevertheless, we do find $A > A_{ad}$ for all 4 cases, which might suggest that (5.3) may often not be necessary.

VI. DISCUSSION

This is the first of two reports on a study of lower bounds on binding energies and on the scattering parameters as listed in Table I. We have given a rather extensive discussion of the physical picture involved in the adiabatic approximation adopted in the formulation using $H_{ad}^{(p)}$. As is clear from the nature of the approximation and also from the examples considered in Sec. V, the bounds we obtained in Secs. II–V on the scattering lengths are expected to be accurate when the projectile mass and one of the target particle

TABLE II. Scattering lengths as functions of the interaction strength G for the two-channel model of Sec. IV. A_{stat} denotes the $L = 0$ scattering length in the static approximation, A is the true value, and A_{ad} is the value in the adiabatic approximation. N_{stat}, N, and N_{ad} denote the corresponding numbers of $L = 0$ composite bound states. For a fixed G, the numbers N_{stat} and N_{ad} are equal to the number of nodes of the associated zero energy scattering wave functions, u_{stat} and u_{ad}; alternatively, these numbers are equal to the number of times the scattering length has passed through $-\infty$ as one increases G from 0 to the value of interest. The theorems that $A_{\text{stat}} > A$ if $N = N_{\text{stat}}$, and $A > A_{ad}$ if $N = N_{ad}$ and Eqs. (2.30) are valid, are seen to be satisfied.

G	N_{stat}	N	N_{ad}	A_{stat}	A	A_{ad}
0.25	0	0	0	0.32	0.18	−0.29
0.50	0	0	0	0.27	0.04	−0.74
0.75	0	0	0	0.21	−0.16	−1.52
1.00	0	0	0	0.15	−0.47	−3.29
1.25	0	0	0	0.09	−0.97	−11.09
1.50	0	0	1	0.01	−1.95	18.69
1.75	0	0	1	−0.07	−4.78	6.35
2.00	0	0	1	−0.15	−95.24	4.22
2.25	0	1	1	−0.25	7.66	3.34
2.50	0	1	1	−0.36	4.23	2.85
2.75	0	1	1	−0.48	3.11	2.53
3.00	0	1	1	−0.62	2.53	2.31

masses are large compared with the masses of the other target particles. Therefore, the formalism is perhaps better suited to an analysis of the ion-atom case than of the positron-atom case, for example. We now discuss briefly various limitations and possible extensions of the theory.

(a) When the simple adiabatic bounds formulated in this paper fail to provide useful results, it is most desirable to be able to improve the bound by a variational procedure. In fact this can be done and will be reported on as a sequence to the present paper.[26]

(b) Since the adiabatic approximation singles out the projectile and treats it differently from the target particles, it is in general difficult to incorporate exchange and rearrangement effects, as in electron-atom and positronium-atom collisions. Consider e^-H scattering, for example. Freezing the second electron at position $\vec{r}_2$, we would find the most general regular solution $\phi_{ad}(\vec{r}_1;\vec{r}_2)$ in the region $r_1 \leq r_2$. The boundary condition would be imposed at $r_1=r_2$. The normal derivative of ϕ would be set equal to zero for the spatially symmetric case, while ϕ itself would be set equal to zero for the spatially antisymmetric case. The method can probably be extended to systems with more than two electrons, but we will not here pursue the matter further; first, the boundary conditions make the computations more difficult than for the positron case, and second, the approximation will not normally be a very good one since we are freezing one particle, an electron, which has the same mass as particles that are allowed to run around freely.

(c) On the other hand, the formalism can describe ion-atom collisions with charge exchange in a very natural way as the adiabatic states $\{\phi_n\}$ are best suited for this purpose. This is in strong contrast with the variational upper bound formulation,[1-5] which fits in better for electron-atom collisions.

(d) Inelastic excitations and other multichannel scattering phenomena at nonzero energies can be treated by appropriate extensions of the present formalism. The modifications required here are closely related to the variational procedure mentioned in (a) and will be reported on later.

APPENDIX A: ADIABATIC POTENTIAL AND EFFECTIVE OPTICAL POTENTIAL

The effective optical potential for elastic scattering at threshold, that is, for $E=E_{T0}$ is given by[27]

$$PU_0P=PV_{00}P+PVG^QVP\,, \tag{A1}$$

$$G^Q=(Q(E_{T0}-H)Q)^{-1}\,, \tag{A2}$$

where

$$P=\psi_{T0}\rangle\langle\psi_{T0}\,,$$

$$Q=1-P\,.$$

The solution of the equation

$$(T+U_0)u_0(\vec{R})=0 \tag{A3}$$

then provides the exact scattering length A, where u_0 is combined with $\psi_{T0}(\vec{r})$ to give

$$P\Psi=\psi_{T0}(\vec{r})u_0(\vec{R})\,, \tag{A4}$$

which is consistent with the boundary conditions (2.5). To compare the problem formulated in (A3) and that in the adiabatic approximation, as given by (2.20), it is useful to analyze the adiabatic potential $\mathcal{V}_0(\vec{R})$. From the definition (2.12) of ϕ_0 and $\mathcal{E}_0(\vec{R})$, we have

$$P(H_T+V-\mathcal{E}_0)P\phi_0=-PVQ\phi_0\,, \tag{A5a}$$

$$Q(H_T+V-\mathcal{E}_0)Q\phi_0=-QVP\phi_0\,. \tag{A5b}$$

Solving for $Q\phi_0$, we obtain

$$Q\phi_0=G_{ad}^QQVP\phi_0\,, \tag{A6}$$

where

$$G_{ad}^Q=[Q(\mathcal{E}_0-H_T-V)Q]^{-1}\,, \tag{A7}$$

and substituting for $Q\phi_0$ in Eq. (A5a), we get

$$P(H_T+V-\mathcal{E}_0+VG_{ad}^QV)P\phi_0=0$$

or

$$P(-\mathcal{V}_0+V_{00}+VG_{ad}^QV)P\phi_0=0\,. \tag{A8}$$

This is not a scattering equation but a form which determines $P\phi_0$ and $\mathcal{E}_0$. Noting that G_{ad}^Q is a *local* operator in the $\vec{R}$ variable, it follows that the entity operating on ϕ_0 in (A8) must vanish, that is, we must have

$$P\mathcal{V}_0P=PV_{00}P+PVG_{ad}^QVP\,. \tag{A9}$$

The second term explicitly exhibits the effects of virtual excitations. Subtracting (A9) from (A1) gives

$$P(U_0-\mathcal{V}_0)P=PV(G^Q-G_{ad}^Q)VP\,. \tag{A10}$$

Now it is easy to show[28] that $B>C>0$ implies $C^{-1}>B^{-1}>0$. If we assume that

$$H_{ad}-E_{T0}\equiv T+\mathcal{V}_0\geq 0\,, \tag{A11}$$

then, with the identifications

$$B=Q(H-E_{T0})Q \quad\text{and}\quad C=Q(H_T+V-\mathcal{E}_0)Q\,,$$

we have $C>0$ by the definition of $\mathcal{E}_0$ and $B>0$ which follows from $C>0$ and (A11). We also have

$$B-C=Q(T+\mathcal{V}_0)Q=Q(H_{ad}-E_{T0})Q\geq 0\,,$$

and it follows that $0 > G^Q > G^Q_{ad}$ and therefore that

$$PU_0P > P\mathcal{V}_0P\,. \tag{A12}$$

With the adiabatic zero-energy wave function $u_{ad}(\vec{R})$ defined by

$$(T+\mathcal{V}_0)u_{ad}(\vec{R})=0\,, \tag{A13}$$

we have, for $\omega \equiv u_{ad}-u_0$, since $Tu_0 = -U_0u_0$,

$$A_{ad} = A - (u_0, (U_0-\mathcal{V}_0)u_0) - (\omega, (T+\mathcal{V}_0)\omega) \leqslant A \tag{A14}$$

using (A11) and (A12). The inequality (A14) is identical to that derived in (2.24).

The discussion given so far has been limited to zero-energy scattering, simply because the inequality (A12) can be proven explicitly only for $E = E_{T0}$. However, we can formally extend our argument which leads to (A14) to the region E somewhat above E_{T0} as follows: from (A1) and (A2), with E_{T0} replaced by E, and from (A9) and (A7), with $\mathcal{E}_0$ replaced by $E+\mathcal{V}_0$, we have

$$\frac{\partial U_Q}{\partial E} < 0 \quad\text{and}\quad \frac{\partial \mathcal{V}_Q}{\partial E} = 0\,; \tag{A15}$$

it follows that (A12) may well not be valid for E large enough, but there will exist a finite region of $E \geqslant E_{T0}$, where (A12) is still valid and thus

$$\eta_{ad} \geqslant \eta \tag{A16}$$

in that region. In general, it is difficult to determine the energy region in which (A12) is valid, but both (A16) and (A12) seem to hold in many cases up to the first excitation threshold, especially when U_0 and $\mathcal{V}_0$ are not too close to each other.

APPENDIX B: BOUNDARY CONDITIONS

The Hamiltonian H_{ad} may differ from H in ways which make it difficult for the associated scattering wave functions to satisfy the same boundary conditions. We now turn to this point.

We begin with e^+He scattering, for which there are no difficulties. The boundary conditions on the true scattering wave function Ψ are that at large e^+-α separation the two electrons are attached to the alpha. On freezing the e^+, the adiabatic bound state wave function ϕ_0 associated with the state of lowest energy will satisfy that condition, as will the adiabatic scattering wave function Ψ_{ad}, and no problems arise.

Consider e^+H scattering, however. The true scattering wave function Ψ has e^- attached to p for large e^+p separation. In the determination of ϕ_0, however, we find ϕ_0 to be symmetric under the reflection of $\vec{R}$ into $-\vec{R}$, where $\vec{R}$ is the e^+p separation; the electron spends half its time near p and half near e^+. This may be disturbing, suggesting as is anyhow obvious that the adiabatic approximation is not too good, but it does not destroy the rigor of the bound. After all, ϕ_0 arises in the determination of $\mathcal{V}_0(R)$, not in the determination of A_{ad}. The wave function whose asymptotic form determines A_{ad} is Ψ_{ad}, not ϕ_0, and Ψ_{ad} is to be determined subject to the appropriate boundary condition, namely, that e^- is bound to p.

We turn now to pH scattering. We have here a true two channel problem for each L for the zero incident energy case under consideration. The two channels can be described in a number of ways. Physically, it is desirable to think of direct and exchange scattering; these correspond to the normal experimental arrangement in scattering. However, since the protons are identical, it is advantageous to work with wave functions Ψ^+ and Ψ^- which are even and odd, respectively, under $\vec{R} \to -\vec{R}$, where $\vec{R}$ is the proton-proton separation, and which represent decoupled channels. (The mixing parameter is zero.) The associated scattering lengths are denoted by A^+ and A^-, respectively. We introduce even and odd adiabatic functions defined by

$$[H_T(\vec{r}) + V(\vec{r},\vec{R}) - \mathcal{E}_n^\pm(R)]\,\phi_n^\pm(\vec{r};\vec{R}) = 0\,,$$

with $\vec{r}$ the separation of the electron and the center of mass of the protons, and with

$$(\phi_n^+, \phi_m^+) = (\phi_n^-, \phi_m^-) = \delta_{nm} \quad \text{for all } \vec{R}\,.$$

The solutions automatically satisfy

$$(\phi_n^-, \phi_m^+) = 0\,.$$

We also have

$$\phi_n^\pm(\vec{r};\vec{R}) \to 2^{-1/2}[\psi_{T0}(\vec{r}_1) \pm \psi_{T0}(\vec{r}_2)]\,, \quad R\to\infty\,,$$

where $\vec{r}_1$ and $\vec{r}_2$ are the separations of the electron from each of the protons, and

$$\mathcal{E}_n^\pm(R) \equiv \mathcal{V}_n^\pm(R) + E_{T0}\,,$$

$$\mathcal{V}_n^\pm(R) \to 0, \quad R\to\infty\,.$$

(We are assuming here that m_e/M_p is vanishingly small.) The adiabatic scattering lengths $A^\pm_{ad}$ defined by Eqs. (2.18)–(2.20), for each L, with $\mathcal{V}_0$ replaced by $\mathcal{V}_0^+$ and $\mathcal{V}_0^-$, respectively, provide the bounds

$$A^+_{ad} < A^+, \quad A^-_{ad} < A^-\,.$$

The bound on A obtained in Sec. V C refers to A^+ and was obtained with the use of $\mathcal{V}_0^+$. We have also looked at the antisymmetric case, using the $\mathcal{V}_0^-$ of Bates and Reid,[20] extrapolated beyond

$R = 20a_0$ by using the polarization potential $-\frac{1}{2}\alpha e^2/R^4$, where $\alpha = \frac{9}{2}a_0^3$ is the polarizability of the hydrogen atom. $\mathcal{V}_0^-$ can definitely support at least one bound state. Whether or not $\mathcal{V}_0^-$ can support a second bound state is touch and go and would require a very precise numerical determination of $\mathcal{V}_0^-$. Since the second state is either just bound or just not bound, only a very careful numerical determination can give a reasonable estimate of A_{ad}^-, which is certainly very large in absolute magnitude.

We can introduce direct and exchange scattering lengths for both the true problem and the adiabatic approximation problem. These are defined by

$$A_{ad}^+ \equiv A_{ad}^{di} + A_{ad}^{ex}, \quad A^+ \equiv A^{di} + A^{ex},$$

$$A_{ad}^- \equiv A_{ad}^{di} - A_{ad}^{ex}, \quad A^- \equiv A^{di} - A^{ex}.$$

We then have

$$A_{ad}^{di} = \tfrac{1}{2}(A_{ad}^+ + A_{ad}^-), \quad A^{di} = \tfrac{1}{2}(A^+ + A^-),$$

$$A_{ad}^{ex} = \tfrac{1}{2}(A_{ad}^+ - A_{ad}^-), \quad A^{ex} = \tfrac{1}{2}(A^+ - A^-).$$

Since $A^{\pm} > A_{ad}^{\pm}$, it follows immediately that

$$A^{di} > A_{ad}^{di} .$$

We cannot obtain a bound on A^{ex} from the above relations. We can, however, obtain the upper bound on A^{di} and upper and lower bounds on A^{ex} if we also have the usual (simpler) upper bounds on $A^{\pm}$.

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