

## Simple asymptotic potential model for finding weakly bound negative ions

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A peculiar class of weakly bound states is discussed. These states are made up of three entities ( $A$ ,  $B$ , and  $C$ ) which have the following property:  $A$  does not form bound states with  $B$  or  $C$  separately but there is a  $BC$  bound state and an  $ABC$  bound state. The term Tango state is suggested to distinguish this class from other weakly bound systems. Two of the mechanisms for forming the  $ABC$  Tango state are discussed. The following systems are predicted to form bound states:  $H_3^-$ ,  $HeH^-$ ,  $NeH^-$ ,  $ArH^-$ , ... and  $Mg_2^-$ ; quantum chemistry calculations very strongly indicate that  $H_3^-$  and  $HeH^-$  form bound states. For the first four species, any exchange of  $D$  for  $H$  will also be a Tango state. [S1050-2947(99)09607-9]

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Weakly bound states of three-body quantum systems are intrinsically interesting as a ‘‘laboratory’’ for correlation because small changes in interaction can cause large changes in the systems’ properties, e.g., size, binding energy, polarizability, etc. In nuclear physics, there are several systems of three particles where  $A$  does not form bound states with  $B$  or  $C$  and  $B$  does not form bound states with  $C$  but  $ABC$  will form a bound state [1–5]. Another class of weakly bound states is the class of Efimov states [6], which occurs when two identical particles have a bound state at zero energy; for this case an infinite number of three-body states occurs for three identical bosons. In molecular physics,  $He_2$  and  $He_3$  form weakly bound states (for some of the isotope combinations) that provide an intense experimental and theoretical challenge for their correct description [7–13].

For a three-object system composed of identical objects, there are four possible bound-state combinations. (i) Neither two- nor three-body bound states are formed. (ii) Two-body bound states are not formed but three-body bound states are formed [14]. (iii) Efimov states are formed. (iv) Both two- and three-body bound states are formed. If the three objects are not identical, a fifth possibility (Tango state) may occur. (v) Object  $A$  will not form bound states with either object  $B$  or  $C$  separately but will form a bound state,  $ABC$ , with both objects together,  $BC$ . The term Tango state is suggested for this type of weakly bound system because it is necessary for the two entities,  $BC$ , to move in a highly correlated manner to form the bound state  $ABC$ . A possible example of this, discussed below, is  $HeH^-$ .  $HeH$  does not have any bound states and  $He^-$  does not have any bound states, although both systems have long-lived *metastable* states. But,  $H^-$  will bind with  $He$  giving a bound state,  $HeH^-$ ,  $1-9\text{ cm}^{-1}$  below the separated atom limit,  $He+H^-$ .

The purpose of this paper is to point out the existence of this class of states and to discuss two mechanisms which cause them to be true bound states (there are probably other mechanisms that are active in different systems than those discussed here). Qualitative calculations are performed in order to derive estimates of the binding energies for simple systems. Comparison with existing quantum chemistry calculations is performed for the two simplest systems; there are no *ab initio* calculations for some of the more complex systems treated here.

Mass-charge correlation will often allow Tango states to form; with this mechanism, the relatively large mass of object  $B$  becomes correlated with the charge of object  $C$  when the state  $BC$  is formed. This mechanism will generate Tango states for all systems  $A$ =noble gas atom,  $B$ =open shell atom that does not bind to  $A$ , and  $C$ =electron. Tango states form with this mechanism because the electron and open-shell atom move together in a highly correlated manner; this can be thought of as an electron with a very large mass. The effective potential for an electron interacting with a noble gas atom has an effective short-range repulsion but a long-range attractive interaction,  $-\alpha/(2r^4)$ , arising from the polarizability of the rare-gas atom; this attractive potential is not enough to give bound states because of the small mass of the electron. The interaction of an open-shell atom with the rare-gas atom has a short-range repulsion and a long-range, attractive van der Waals interaction; unfortunately, the van der Waals interaction is usually too weak to give bound states. By attaching the electron to the open-shell atom, the combination gives the more attractive polarizability interaction,  $-\alpha/(2r^4)$ , with the heavier mass of the atom.

This combination of properties is enough to ensure that  $HeH^-$  will form a true bound state [15]. In fact,  $H^-$  and  $D^-$  form bound states with all of the rare-gas atoms. Since this is the least likely combination (because of the low reduced mass), it is expected that any negative ion will form at least one bound state with any rare-gas atom. For example, the reduced mass in the  $HeLi^-$  system is three times larger than in the  $HeH^-$  system; as another example, the  $NeNa^-$  system has a reduced mass over 10 times larger than the  $HeH^-$  system and has a large number of bound vibrational states. Another system that forms Tango states using this mechanism is  $H_3^-$ ,  $H_2D^-$ ,  $D_2H^-$ , and  $D_3^-$ .  $H_3^-$  can be thought of as the bound state of  $H_2$  and  $H^-$  [16].

Model calculations can be performed to discover which Tango states are likely to be formed. The primitive calculations that follow serve as a strong indicator of Tango states but do not replace full quantum-chemistry-type calculations or experimental measurements. The model calculation is meant to test whether  $H^-$  will form bound states with different rare-gas atoms. To accomplish this task, it is necessary to calculate the Born-Oppenheimer potential curve with the distance between the proton and the rare-gas nucleus serving as

the adiabatic variable. This potential will be zero by definition when the  $\text{H}^-$  and the rare-gas atom are infinitely far apart. Because the potential curve only depends on the distance between the  $\text{H}^-$  and the atom, the  $\text{H}^-$  is placed at the origin and the atom will be on the positive  $z$  axis a distance  $R$  from the origin.

The key part of the interaction is that the electron is loosely bound to the H atom with all other electrons being tightly bound. The  $\vec{r}$  will be used to denote the distance of the loosely bound electron from the proton. The loosely bound electron's wave function can be approximated by  $\psi(\vec{r}) = F(r)/\sqrt{4\pi r^2}$ , where  $F(r) = N \exp(-\kappa r)$  for  $r > 1$  a.u. and  $F(r) = N(br + cr^2 + dr^3)$  for  $r < 1$  a.u. with  $b, c,$  and  $d$  chosen so  $F(r), F'(r),$  and  $F''(r)$  are continuous at  $r = 1$  a.u.;  $N$  is a normalization constant,  $N \sim \sqrt{2\kappa}$ , and the constant  $\kappa = 0.235$  a.u.  $= \sqrt{-2E_b}$ , where  $E_b$  is the binding energy of  $\text{H}^-$ . The effect of having the  $r < 1$  a.u. dependence in  $F(r)$  is to increase the size of the normalization constant from the value  $\sqrt{2\kappa}$ . Since the  $\text{H}^-$  never gets closer to the rare-gas atom than 1 a.u., this has the effect of slightly increasing the strength of the repulsive contact interaction.

The two main terms in the Born-Oppenheimer potential arise from the interaction of the loosely bound  $\text{H}^-$  electron with the rare-gas atom. The distance between the proton and the rare-gas atom will be denoted  $\vec{R}$ . This interaction has two parts: (i) a repulsive contact potential term

$$U_c(R) = \langle \psi | V_c | \psi \rangle = -2\pi a \psi^2(\vec{R}) = -\frac{a}{2R^2} F^2(R), \quad (1)$$

where  $a = \tan(\delta_0)/k$  as  $k \rightarrow 0$  with  $\delta_0$  the  $s$ -wave electron-rare-gas atom phase shift at kinetic energy  $E = k^2/2$ , and (ii) an attractive polarizability potential  $U_p = \langle \psi | V_p | \psi \rangle$ . The polarizability potential has the asymptotic form  $-\alpha/(2w^4)$ , where  $w = |\vec{r} - \vec{R}|$  is the distance between the electron and the rare-gas atom. In order to make the integral tractable,  $V_p(w) \equiv -(\alpha/2)w^2/(w^2 + w_0^2)^3$ , where  $w_0$  is a distance where the potential changes from  $w^2$  to its correct asymptotic  $1/w^4$  behavior. With this potential, the integral over angles can be performed analytically leaving

$$U_p(R) = -\frac{\alpha}{2} \int_0^\infty dr F^2(r) [1 - \eta(r)\xi(r)] \eta(r), \quad (2)$$

where the functions  $\eta(r) = [(r^2 + w_0^2 - R^2) + 4R^2 w_0^2]^{-1}$  and  $\xi(r) = w_0^2(r^2 + w_0^2 + R^2)$ . The integration in Eq. (2) is carried out numerically for each  $R$  needed for the potential curve. The full Born-Oppenheimer potential is  $U = U_c + U_p$ . The

TABLE I. Scattering length ( $a = \tan[\delta_0]/k$ ), polarizability ( $\alpha$ ), and reduced mass ( $\mu$ ) needed for the calculation of  $\text{H}^-$  plus neutral Tango state.

Neutral	$a$ (a.u.)	$\alpha$ (a.u.)	$\mu$ (a.u.)
He	-1.48	1.322	1470
Ne	-1.07	2.38	1750
Ar	-1.50	10.77	1795
$\text{H}_2$	-2.14	4-5	1225

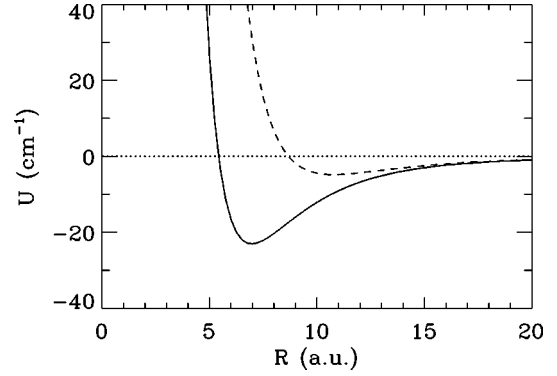


FIG. 1. Born-Oppenheimer potential for the  $\text{HeH}^-$  system for  $w_0 = 1$  a.u. (solid line) and  $w_0 = 3$  a.u. (dashed line).

reduced mass in the Hamiltonian is  $\mu = (M_A + M_B)M_C/(M_A + M_B + M_C)$ . The parameters used for the different rare-gas atoms are given in Table I.

The electron-rare-gas phase shifts are calculated without including the polarizability potential [17] since this interaction term is included in  $U_p$ . The polarizabilities for the rare-gas atoms are taken from Ref. [18]. The only parameter that is not determined is  $w_0$ . As  $w_0$  increases, the size of  $U_p$  decreases, which will decrease the binding energy. The procedure adopted here is to let  $w_0$  take two values, 1 a.u. and 3 a.u. Since the size of the rare-gas atoms is less than  $\sim 1$  a.u., the binding energies from these two values of  $w_0$  will provide rough upper and lower bounds on the binding energy. In fact, the value  $w_0 = 3$  a.u. is unrealistically large, which will give an unrealistically small polarizability interaction; this large value was chosen so that if bound states result even with an unrealistically weak polarizability potential, we can have confidence that bound states would result in the true potential.

In Fig. 1, the Born-Oppenheimer potential for the  $\text{HeH}^-$  system is shown for the two cases  $w_0 = 1$  a.u. (solid line) and  $w_0 = 3$  a.u. (dashed line). It is clear that the potential has a minimum whose position and depth strongly depend on  $w_0$ . Nevertheless, both potentials (even the unrealistically large  $w_0 = 3$  a.u.) contain bound states. In Table II, the number of bound ( $J=0$ ) states and the binding energy are presented for several Tango states for  $w_0 = 1$  a.u. and for  $w_0 = 3$  a.u. Substituting  $D$  for  $\text{H}$  will also be a Tango state because the Born-Oppenheimer potential curve will be the same and the reduced mass increases. There are several states which are so tightly bound, the model potential fails ( $\text{NeH}^-$  for  $w_0$

TABLE II. Binding energy,  $E_b$ , and number  $n$  of bound  $J=0$  states for different systems;  $w_0$  is the rough distance at which the asymptotic form of the polarizability potential begins.

System	$w_0$ (a.u.)	$E_b$ ( $\text{cm}^{-1}$ )	$n$	$w_0$ (a.u.)	$E_b$ ( $\text{cm}^{-1}$ )	$n$
$\text{HeH}^-$	1	9	2	3	0.9	1
$\text{NeH}^-$	1	640	5+	3	12	2
$\text{ArH}^-$	1	20 000	5+	3	290	5+
$\text{H}_3^-^a$	3	30	3	5	8	2
$\text{H}_3^-^b$	3	16	3	5	4	2

<sup>a</sup> $\alpha = 5$  a.u.

<sup>b</sup> $\alpha = 4$  a.u.

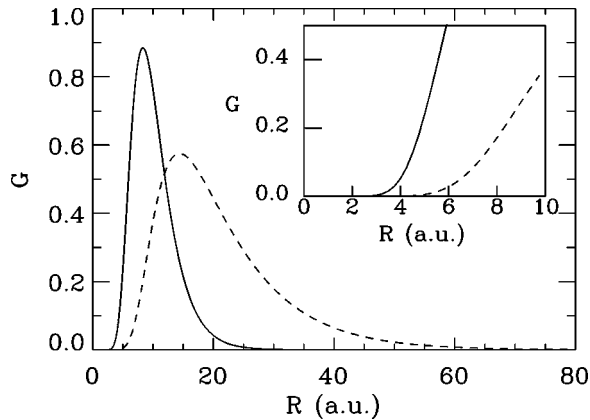


FIG. 2. Radial part of the nuclear wave function for  $w_0 = 1$  a.u. (solid line) and  $w_0 = 3$  a.u. (dashed line). Inset is a blowup of the small  $R$  wave function for  $w_0 = 3$  a.u.

$= 1$  a.u. and  $\text{ArH}^-$  for both values of  $w_0$ ); these states will certainly be bound but the precise value of the binding energy is not certain because the atoms overlap too much and the core electron of the H interacts with the electrons on the rare-gas atom. In Fig. 2 is a plot of the radial part of the  $\text{HeH}^-$  ground-state wave function,  $\Psi(\vec{R}) = G(R)/\sqrt{4\pi R^2}$ , with a blow up of the small- $R$  region; the solid line is for the potential with  $w_0 = 1$  a.u. and the dashed line is for the potential with  $w_0 = 3$  a.u. This shows that the inner tightly bound electrons in He and H do not overlap at all, so all of the potential is determined by the loosely bound  $\text{H}^-$  electron interacting with the He atom. In Ref. [15], large quantum chemistry calculations gave a value of roughly  $0.6 \text{ cm}^{-1}$  for the binding energy of  $\text{HeH}^-$ .

The results presented here arise from simple calculations, so it is necessary to assess the reliability of the approximations. Using first-order perturbation theory is a good approximation as long as the ratio of the  $U_c + U_p$  to the binding energy of H (roughly  $6000 \text{ cm}^{-1}$ ) is small; this ratio indicates that the corrections for  $\text{HeH}^-$  and  $\text{NeH}^-$  will be less than 10%. Another simplification involves using approximations for the  $U_c$  and  $U_p$  terms. The approximation of  $U_c$  through a contact term will be quite accurate since the prefactor of the contact term uses the *exact* phase shift. This method has a relative error proportional to the kinetic energy of the electron scattering from the potential; since the electron “scattering” from the rare-gas atom is the outer electron of the  $\text{H}^-$  ion (kinetic energy of  $-0.03$  a.u.), errors of a few percent are expected. The main source of error is in the calculation of  $U_p$  because a simple model potential was chosen for the polarizability interaction. As can be seen in Table II, reasonable choices of  $w_0$  can change the binding energy by an order of magnitude. This deficiency can be mended by using an optical potential for the polarizability potential.

In Tables I and II, parameters for  $\text{H}_2$  and  $\text{H}^-$  were also presented. The model presented here does not work very well for this system because  $\text{H}_2$  is not spherically symmetric; the potential for  $\text{H}_2\text{H}^-$  is anisotropic from the quadrupole potential and from the polarizability potential which depends on the angle between the  $\text{H}^-$  and the  $\text{H}_2$  internuclear axis. However, we can use the model for this system to check whether or not bound states are formed if we use a potential that is everywhere *greater* than this anisotropic potential. If

the binding energy is large, even for unrealistically large choices of  $w_0$  and small values for  $\alpha$ , then we would expect that  $\text{H}_3^-$  is bound; the anisotropic interactions increase the binding energy.

The scattering length was obtained from the sum of the eigenphase shifts of Ref. [19] based on the method described in Ref. [20]; exchange effects are treated exactly using the linear-algebraic method, as describe in Ref. [21]. The binding energies of Table II indicate that  $\text{H}_3^-$  forms at least one bound state. Further, there will be long-lived resonance states attached to each of the rotational states of  $\text{H}_2$ . These results are in good agreement with the quantum chemistry calculations of Ref. [16], where the binding energy was calculated to be  $\sim 70 \text{ cm}^{-1}$ .

An interesting aspect of  $\text{H}_3^-$  is its interaction with slow, positively charged ions. Because  $\text{H}^-$  is very weakly bound to  $\text{H}_2$ , a slow proton (for example) will have a very large cross section for capturing the  $\text{H}^-$  from the  $\text{H}_2$ . The capture cross section can be estimated from  $\sigma \sim \pi r_s^2$ , where  $r_s$  is the farthest distance that a proton can classically strip the  $\text{H}^-$  from the  $\text{H}_2$ ; this distance can be estimated by noting that  $r_s^2 \approx 1/E_s$ , where  $E_s$  is the electric field needed to strip the  $\text{H}^-$  from the  $\text{H}_2$ . The maximum value of the potential  $-\alpha/(2R^4) - E_s R$  is  $-1.25E_s^{4/5}(2\alpha)^{1/5}$ . Setting this equal to the binding energy gives  $\sigma \sim 26\alpha^{1/4}/|E_b|^{5/4}$ , where  $E_b$  is the binding energy. Using  $E_b = 30 \text{ cm}^{-1}$  gives a capture cross section  $2 \times 10^6$  a.u.

A second mechanism that allows the formation of Tango states is dielectronic relaxation. This mechanism will sometimes generate Tango states for the system  $A=\text{electron}$ ,  $B=\text{atom}$ , and  $C=\text{closed shell atom}$ . The electron does not form bound states with either atom but the two atoms form a loosely bound molecular system with the atoms separated by a distance  $R$ . Although the electron does not form a bound state with atom  $B$ , it is assumed that it forms a resonance state at a positive electron energy of  $E_r$ . If the resonance state has nonzero orbital angular momentum,  $L$ , then the energy of the  $L\Pi$ ,  $L\Delta$ , ... states of the  $ABC$  system will be  $\sim E_r - \alpha/(2R^4)$ , where  $\alpha$  is the dipole polarizability of the closed shell atom,  $C$ . The nonzero value of  $\Lambda$ , the projection of the total angular momentum on the internuclear axis, is important because this forces the electron wave function to have a node on the axis; this greatly reduces the effect of the repulsive short-range  $AC$  interaction, thus allowing the energy to be substantially lower than it would be if  $\Lambda = \Sigma$ . If  $E_r < \alpha/(2R^4)$ , then a Tango state may be formed; the electron cannot leave the system because it gains energy  $E_r$  when leaving atom  $B$  but must give an amount  $\alpha/(2R^4)$  to atom  $C$ , which it cannot do if  $E_r < \alpha/(2R^4)$ . This mechanism is similar to that discussed in Ref. [22] in the context of vibrationally inelastic electron-molecule scattering in a molecular solid.

The  $^2P^o$  resonance state of  $\text{Mg}^-$  can serve as an example of dielectric relaxation as a mechanism to generate Tango states ( $\text{Mg}_2^-$ );  $\text{Mg}^-$  does not form bound states but  $\text{Mg}_2^-$  does form bound states. The  $\text{Mg}^- \ ^2P^o$  resonance state is at an electron energy of  $0.166 \text{ eV} = 0.0061$  a.u. If the projection of the angular momentum of this state on the internuclear axis is  $\pm 1$ , there will be a node of the wave function on the axis. Since the electron attached to one of the Mg does not

overlap strongly with the other Mg, the ground-state energy will be roughly the resonance energy plus the energy for the polarizability interaction. The polarizability of Mg is  $\sim 70$  a.u. This means that if the internuclear separation is less than  $\sim (\alpha/2E_r)^{1/4} = 8.7$  a.u., the total electronic energy of  $\text{Mg}_2^-$  will be less than the total electronic energy of  $\text{Mg}_2$ . The internuclear distance of  $\text{Mg}_2$  is 3.9 a.u. This strongly indicates that  $\text{Mg}_2^-$  will form a Tango state.

It is a simple exercise to find the largest possible internuclear distance that will allow a Tango state to form. Using the polarizabilities of Ref. [18],  $\text{NeMg}^-$  will form if the internuclear distance is less than  $\sim 3.7$  a.u.,  $\text{ArMg}^-$  will form if the internuclear distance is less than  $\sim 5.4$  a.u.,  $\text{KrMg}^-$  will form if the internuclear distance is less than  $\sim 6.0$  a.u., and  $\text{XeMg}^-$  will form if the internuclear distance is less than  $\sim 6.8$  a.u. Probably several of these systems will form Tango

states. (It is possible that these systems might form halo states if the neutral molecule does not form bound states. For example, it is very likely that  $\text{XeMg}^-$  will form bound states even if  $\text{XeMg}$  does not.)

Two different mechanisms for the formation of weakly bound states have been identified. This allows simple calculations to answer whether or not certain systems will form bound states. This is a remarkable circumstance since large calculations are usually needed to determine whether a weakly bound system is truly bound.

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