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Calculations of some weakly bound diatomic molecular negative ions

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We examine the existence of stable bound states of some diatomic molecular ions where the neutral molecule itself is either unbound or barely bound. Two bound states have been found for the HeH^- ion even though HeH is known to be unbound. We have found no bound states for ${He_2}^-$ even though $^4He_2$ is known to have one bound state. The predicted binding energies for HeH^- are of the order of 1 K and depend sensitively on the isotope combinations. Other weakly bound negative ions such as NeH^- and ArH^- have also been investigated. These weakly bound molecular ions are good candidates for cold collision experiments. [S1050-2947(99)01509-7]

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I. INTRODUCTION

The search for weakly bound simple atomic and molecular species is a fascinating subject. The stability of these systems depends sensitively on the interaction potentials and the relative motion of the particles which is generally understood as the correlation or the many-body effects of the system. Quantum symmetry is also known to play an essential role [1] and the stability of the system depends critically on the masses of the constituent particles. Simple well-known rules for the binding of molecules which are valid for the more tightly bound systems cannot be applied to draw conclusions for the weakly bound molecular systems. For example, He_2 dimers and He_3 trimers have been predicted to exist [2–8] and have also been confirmed experimentally [9–12], yet their existence cannot be anticipated based on the conventional theory of chemical bonding.

For three identical particles A_3, there are two peculiar situations that have been well investigated theoretically, especially in nuclear physics. One is the so-called halo states (or the Borromean states) which are defined for the bound states of a three-body system A_3 when its two-body system A_2 does not have any bound states [13,14]. Another is the Efimov states [15,16] where the three-body system supports an infinite number of bound states when the two-body system supports only one bound state with zero binding energy. No known examples of halo states or Efimov states for three identical particles have been found in atomic and molecular systems, although the second state of the helium trimer appears to have properties similar to those of an Efimov state [2,17,18].

When the three particles are not all identical, there are new possibilities for the existence of stable two-body and three-body bound states. For the Coulomb three-body systems an extensive literature exists on the condition for the stability of the three-body systems [19]. In this article we address examples from the ''standard'' simple diatomic molecular systems, in particular, diatomic molecular anions which can be approximated as three-body systems consisting of two atoms and one electron. These three-body systems are denoted as ABe, where e stands for the electron and A and B are atoms which can be identical or different. We will study very diffuse or weakly bound systems only where the internal structures of A and B are not expected to be important. Thus the three-body system is modeled to consist of pair interactions between $(A+B)$, $(A+e)$, and $(B+e)$. Each pair interaction has an attractive part but the strength may be too weak to form any bound states, or just strong enough to support one or a few bound states. Consider the specific example, $(He+H+e)$, or HeH^-. The pair $(He+H)$ or $(He+e)$ have no stable bound states, but $(H+e)$ has one bound state, the H^- ion, with binding energy of about 0.75 eV. The question we want to address is whether $(He+H+e)$ together can form some bound states, or, equivalently, is HeH^- stable? As a second example, consider $He+He+e$. The pair $(He+He)$ is known to have one bound state with binding energy of about one millidegree Kelvin [2,6,8], but $(He+e)$ has no bound states. The question is whether $(He+He+e)$ can form stable ${He_2}^-$ bound states.

The existence of stable bound states for HeH^- has been predicted recently by Bendazzoli *et al.* [20]. They performed full *ab initio* calculations for the Born-Oppenheimer (BO) potential curves including all the four electrons in the system using the general quantum chemistry package. Since the wave function of the outermost electron is rather diffuse and the primitive orbitals are Gaussian functions, the calculations have to be carried out with a very large basis set. They predicted two bound states, with energies at about 0.8 K and 0.1 K, respectively, below the He + H^- dissociation threshold. Since the binding energies are very small, they showed that the results depend sensitively on the basis functions used. In this paper we do not perform pure *ab initio* calculations. Instead we model the HeH^- ion as a three-body system and calculate the binding energies also within the BO approximation. The effective interactions between each pair of particles are taken from what we consider to be the best available in the literature. From the calculated BO potential curves we then calculate the binding energies for the HeH^- ions, including the isotope dependence. Similar calculations have also been carried out for the NeH^- and ArH^- systems which are shown to have many more bound states.

We also performed calculations to look for the possible existence of stable ${He_2}^-$ ions. Interestingly one cannot use the BO approximation to calculate the potential curves for this system. In the BO approximation the dissociation limit consists of an atom and a negative ion. However, there is no

TABLE I. Comparison of phase shifts calculated from the model potentials with those from the accurate *ab initio* calculations for the e-H and e-He collisions. Only the low energy phase shifts are shown here. (a) From the model potential of Laughlin and Chu [21]. (b) Schwartz [23]. (c) From the model potential of Reid and Wadehra [24]. (d) Variational calculation of Nesbet [25].

Energy (a.u.)	Phase shift	
e-H	(a)	(b)
0.05	2.5532	2.5530
0.020	2.0666	2.0673
0.045	1.6970	1.6964
e-He	(c)	(d)
0.021	2.8374	2.8672
0.045	2.6984	2.7386
0.055	2.6519	2.6939
0.080	2.5590	2.6029

He^- bound state. Instead, He_2 has a bound state such that $He_2{}^-$ would be dissociated to an electron and a helium dimer. For this system we performed the calculations in hyperspherical coordinates within the adiabatic approximation. The resulting hyperspherical potential curve does dissociate to the correct limit of an electron and a He_2 dimer. From the calculated hyperspherical potential curve we conclude that there are no stable $He_2{}^-$ ions for any isotope combinations.

II. THEORETICAL METHODS AND RESULTS

A. Calculations of the bound states of HeH^- anions

To calculate the BO potential curves for the HeH^- ion we first have to adopt the best model potentials describing the interactions between the pairs of particles: e-H, e-He, and He-H. For the model potential between the electron and the atomic hydrogen, we adopted the one from Laughlin and Chu [21]. This potential was fitted to reproduce the binding energy of the ground state of H^- and the low energy ${}^1S^e$ elastic scattering phase shifts and has been used to study the multiphoton detachment of H^-. Table I compares the phase shifts obtained from this model potential with those obtained from the accurate variational calculations of Schwartz [23]. For the model potential between the electron and the helium atom, we adopted the one from Reid and Wadehra [24]. The quality of this potential is checked by comparing the elastic phase shifts calculated from this potential with those from the accurate variational calculations of Nesbet [25] (see Table I). For the effective interaction between He and H, we adopted the potential from Meyer and Frommhold [26]. This potential was obtained from quantum chemistry calculation and fitted and adjusted so that it describes accurate He-H scattering data at thermal energies. One comment has to be made on the e-He model potential: This potential supports an unphysical bound state at $E=-0.316$ a.u. This unphysical state is viewed as the $1s$ state of the helium ion which is not excluded from the solution within the model potential approach.

Within this one-electron model we assume that the HeH^- potential surface consists of the pair interactions only and there are no ''three-body'' forces. This is expected to be a reasonable model for the diffuse molecular system where the core electrons in He and in H are well separated and thus assumed to be unperturbed. This is also the model adopted in practically all studies in helium trimer studies. For the latter, the ''three-body force'' has been shown to affect less than 1% of the ground-state energy [22].

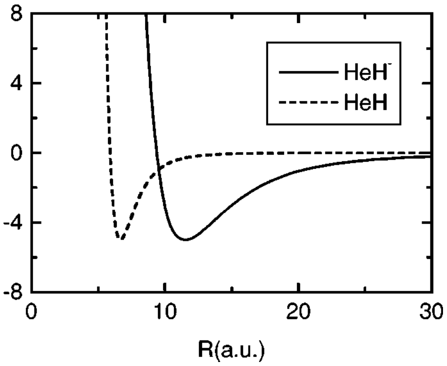

FIG. 1. The ground-state Born-Oppenheimer potential curves for HeH and HeH^-. The former is adopted from the suggested data of Meyer and Frommhold [26] and the latter is obtained from the present calculation.

We solved the one-electron diatomic molecular ion problem within the BO approximation. Using spheroidal coordinates the resulting two-dimensional eigenvalue equation at each internuclear separation R is solved using two-dimensional B-spline basis functions. This method has been used previously to obtain very accurate potential curves for the $H_2{}^+$ ions [27] and we followed essentially the same numerical procedure for the present system.

In Fig. 1 we show the calculated HeH^- potential curve and compare it with the HeH potential curve of Meyer and Frommhold [26]. Note that HeH has an attractive potential well with the minimum at $R=6.66$ a.u. where the depth is 4.97 cm^{-1}. The calculated HeH^- potential has the minimum at $R=11.5$ a.u. and the well depth of 4.99 cm^{-1}. While the well depths do not differ much between the two systems, the position of the minimum is shifted and the width of the potential well for HeH^- is much broader. The difference is due mostly to the asymptotic potentials. For HeH, the interaction between two neutral atoms at large distance is described by a van der Waals potential which decreases as $1/R^6$ at large R. For HeH^-, the system separates into He and H^-, thus the asymptotic interaction is the induced dipole potential which decreases at a slower $1/R^4$ rate. Thus the potential well for HeH^- is much broader and the increased strength permits the formation of stable bound states for HeH^-, in contrast to the HeH potential which supports no bound states.

From the calculated BO curve for HeH^-, we looked for the possible existence of bound states. For these weakly bound systems, the binding energies depend very sensitively on the mass of the constituent particles. For ${}^4He\,{}^1H^-$, we found one bound state at 1.37 K for $J=0$ and one bound state at 0.566 K for $J=1$. ($1\ K=0.695\,038\,7\ cm^{-1}$ $=8.617\,385\times10^{-5}$ eV.) We found no other bound states. In Fig. 2 we show the vibrational wave functions for these two states. The sizes of these two states, as measured by the expectation values $\langle R\rangle$, are 17.9 a.u. and 20.2 a.u., respectively. They are definitely among the largest diatomic mo-

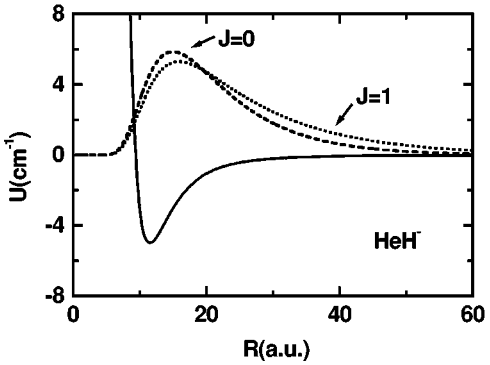

FIG. 2. The vibrational wave functions for the $J=0$ and $J=1$ states for the potential curve given in Fig. 1 for the $^4\mathrm{HeH}^-$ system.

lecular ions. Their large size is related to the small binding energies.

The existence of stable bound states for HeH^- has been predicted earlier by Bendazzoli *et al.* [20] where they obtained the lowest BO potential curve using the general quantum chemistry codes. While their approach is essentially exact in principle, the *ab initio* calculation including all the four electrons is a much more difficult and challenging task. Our model potential calculation certainly provides an independent check on their results. The binding energies obtained from Bendazzoli *et al.* range from 0.4344 K to 1.3136 K for $J=0$ and from 0.0005 K to 0.5255 K for $J=1$ depending on the basis sets used. However, we agreed with their conclusion that there is only one bound state each for $J=0$ and $J=1$, respectively.

Within the BO approximation we also have calculated the binding energies of the different isotope combinations for the HeH^- systems. The binding energies for these different isotope combinations are listed in Table II and compared to the results of Bendazzoli *et al.* It should be pointed out that the results quoted from Bendazzoli *et al.* were obtained using one of their better basis sets (from Table 6 of that paper).

We did not calculate the adiabatic corrections to the BO potential energy curve. This was estimated by Bendazzoli *et al.* and found to be smaller than 0.01 K to the BO curve near the potential minimum. Such a small correction is not important at the level of accuracy pursued in this paper.

As pointed out earlier, there is an unphysical He^- bound state in the present model potential approach. In Fig. 3 we show the first three BO potential curves calculated for HeH^-. The second curve was used to obtain the results reported above. The first curve, which approaches the He^- ‘‘bound state,’’ has the potential minimum at about 2 a.u. and it is well separated from the curve of interest (the second curve). Note also that the second curve appears very shallow in the scale shown in Fig. 3. The third curve, as shown in finer scale in the inset, is completely repulsive and supports no bound states. Thus there are no other stable bound states for HeH^- than the two reported above.

TABLE II. Binding energies for HeH^- anions. There are two bound states ($J=0$ and $J=1$) for each isotope combination listed. The quantum chemistry (QC) calculations are from Bendazzoli *et al.* [20]. The binding energies are given in degrees Kelvin.

	$J=0$		$J=1$	
	Present work	QC	Present work	QC
$^4\mathrm{He}\,^1\mathrm{H}^-$	1.37	0.575	0.566	0.1
$^4\mathrm{He}\,^2\mathrm{H}^-$	2.23	1.1017	1.26	0.6639
$^3\mathrm{He}\,^1\mathrm{H}^-$	1.26	0.5156	0.445	0.0085
$^3\mathrm{He}\,^2\mathrm{H}^-$	2.06	0.9898	1.40	0.5284

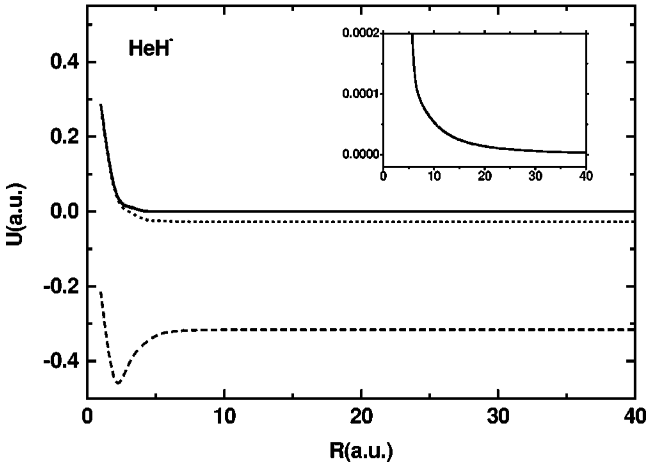

FIG. 3. The three lowest BO potential curves calculated for the HeH^- system using the model potentials described in the text. The lowest curve results from the unphysical bound state in He^- predicted by the model potential adopted. This lowest curve is ignored. The second curve is the one shown in Fig. 1 in an expanded scale. The third curve is completely repulsive. The inset gives an expanded view of the third curve.

B. Search for possible bound states in He_2^-

The existence of He_2 was not expected based on the common chemical bonding mechanisms. However, many theoretical calculations have predicted the existence of one and only one bound state for $^4\mathrm{He}_2$, with binding energy of about 1.3 mK [6–8]. These calculations further showed that other mass combinations of the helium dimers do not have any bound states. While the binding energy of $^4\mathrm{He}_2$ has never been directly measured, its existence has been confirmed in atom interferometer experiments [9,10] and its size has also been deduced from the experiment to be 122 ± 20 a.u. [12], which is in good agreement with the theoretical value of about 100 a.u.

Having established the existence of $^4\mathrm{He}_2$, we ask if an electron can attach itself to such a diffuse system to form a bound state. It is known that stable He^- ions do not exist. Thus any bound states of He_2^- would dissociate into an electron and a He_2 molecule. This is an interesting molecular system where the standard Born-Oppenheimer approximation cannot be applied since the dissociation limit is not characterized by large internuclear separations, but rather by the large distance between an electron and a molecule.

We investigated this system using hyperspherical coordinates in the adiabatic approximation. This method was used previously to study helium trimers [2] and other weakly bound systems such as $\mathrm{He}_2\mathrm{Li}$ and $\mathrm{He}_2\mathrm{Na}$ [28], as well as the bound states formed by a positron and Li [29]. Using mass-weighted hyperspherical coordinates as described in Esry *et al.* [2], we calculated the hyperspherical potential curves

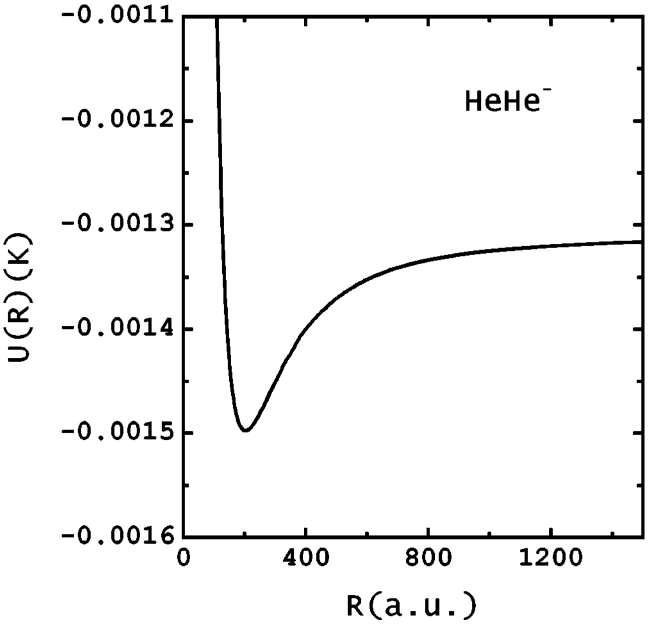

FIG. 4. The hyperspherical potential curve for the $^4\mathrm{He}_2{}^-$ system. The potential is not attractive enough to support any bound states.

in the adiabatic approximation. *B*-spline basis functions were used to solve the equations involving hyperangles. For the present two heavy and one light three-body system, the potential surface has wells concentrated in a small range of hyperangles. The parameters in the *B*-spline functions were carefully adjusted to check the convergence. Since the convergence is more difficult to achieve at large hyperradius where the eigensolutions are more localized, we know the converged result is accurate when it reproduces the asymptotic energy (which is the binding energy of $^4\mathrm{He}_2$).

For the $^4\mathrm{He}_2{}^-$ system, the electron-helium model potential used is the same as before. The He-He model potential was obtained from Aziz and Slaman [30]. Other newer potentials have been proposed recently [31,32], but they do not differ much from the one employed here.

The hyperspherical potential curve that approaches the He_2 limit asymptotically is shown in Fig. 4. The potential curve has the minimum at the hyperradius $R=203$ a.u. From this potential curve we searched for the bound states, but none was found. Note that the potential well is very shallow. We calculated the phase

$$\Phi=\int_{r_c}^{+\infty}\{2[E-U(R)]\}^{1/2}dR,$$

where E is taken to be the energy at the dissociation limit and $r_c=127.8$ a.u. is the inner classical turning point. This integral was calculated to be 0.0094π, which is much smaller than the value $3\pi/4$ needed, according to the WKB theory, to support a bound state. Clearly this conclusion will not change for any reasonable modification to the model potential used and we can conclude that there are no bound $\mathrm{He}_2{}^-$ ions for any isotope combinations. (Note that $\mathrm{He}_2{}^-$ does exist when the He is in the excited states.)

It is interesting to examine the electron's distribution, or its relative position with respect to the two helium atoms as the mass-weighted hyperradius is varied. In Fig. 5 we show the averaged internuclear separation $\langle\rho_1\rangle$ and the averaged distance $\langle\rho_2\rangle$ of the electron measured from the midpoint of the interatomic line. For a typical stable molecule, the average values $\langle\rho_1\rangle$ and $\langle\rho_2\rangle$ are of the same order. The results in Fig. 5 show that $\langle\rho_2\rangle$ is much larger than $\langle\rho_1\rangle$. Furthermore, at large hyperradius $\langle\rho_1\rangle$ remains nearly constant, while $\langle\rho_2\rangle$ scales linearly with R. This implies that the electron on the average is far away from the He_2 molecule. The electron does not stay close to the two helium atoms to form bound states.

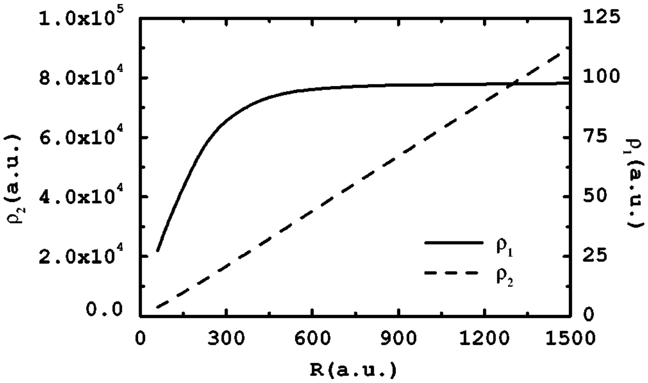

FIG. 5. (a) The average distance $\langle\rho_1\rangle$ between the two helium atoms at each hyperradius R. For small hyperradius, $\langle\rho_1\rangle$ grows with R, but at large hyperradius the $\langle\rho_1\rangle$ is nearly at a constant value of about 90 a.u. which is roughly the distance between the two helium atoms for the He_2 molecule. (b) The average distance of the electron from the midpoint of the line connecting the two helium atoms. Note that $\langle\rho_2\rangle$ grows linearly with R, indicating that the electron is moving further out with the distance between the two helium atoms more or less fixed as the hyperradius is increased.

C. NeH$^-$ and ArH$^-$ anions

We have also calculated the binding energies of the NeH$^-$ and ArH$^-$ anions within the BO approximation. To do these calculations we first need to adopt the effective potentials between each pair of particles. For the effective interaction potentials between Ne-H and between Ar-H, we used the potentials given by Tang and Toennies [33]. These potentials are more attractive than the potential for HeH. As shown in Fig. 6(b) the well depth for NeH is 12.20 cm^{-1} and for ArH is 38.34 cm^{-1}, which are to be compared to the depth of 4.97 cm^{-1} for HeH. Due to the deeper potential wells and the larger masses these two systems can support bound states. For ^{20}NeH there is one $J=0$ bound state with binding energy at -5.42^{-2} K. For ^{40}ArH, there exist three bound states: at -12.09 K for $J=0$, at -9.411 K for $J=1$, and at -4.260 K for $J=2$.

For the interaction potentials between e-Ne and between e-Ar, we used the ones from Reid and Wadehra [24]. The interaction potential between e-H was again adopted from Laughlin and Chu. With these effective pair interactions chosen we solve the BO potential curves for the NeH$^-$ and ArH$^-$ systems and the results are shown in Fig. 6(a). Note that the potential wells for these two systems are significantly much deeper as compared to HeH$^-$. The well depth for NeH$^-$ is 613 cm^{-1} and for ArH$^-$ is 1034 cm^{-1}. The

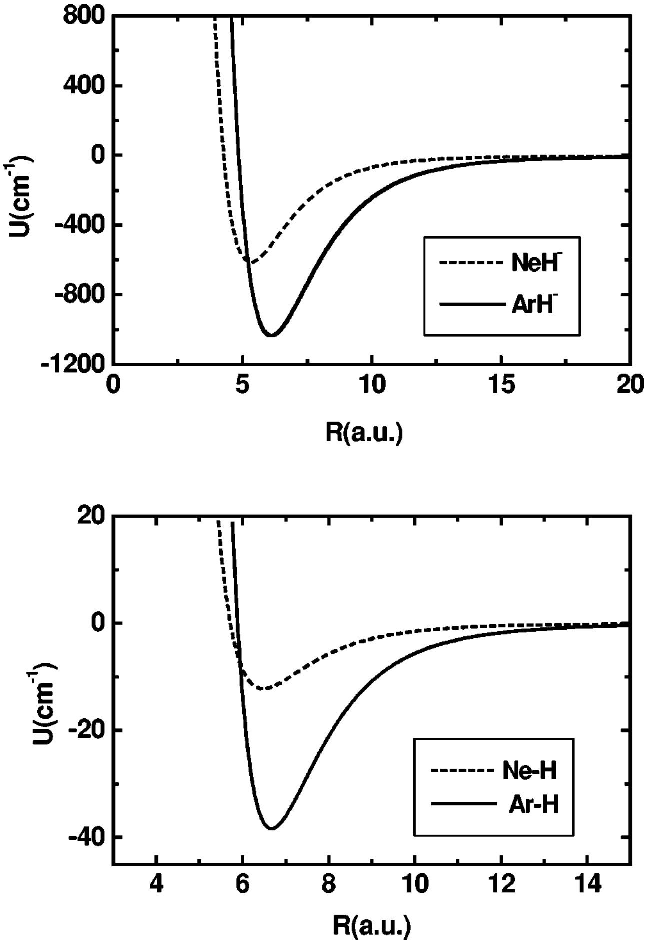

FIG. 6. (a) The calculated BO potential curves for the ground state of NeH$^-$ and of ArH$^-$. (b) The empirical potential curves between Ne-H and between Ar-H.

deeper wells are partly due to the larger dipole polarizabilities for Ne (2.66 a.u.) and Ar (11.1 a.u.) than for He (1.38 a.u.). However, the large increase in the well depth is mostly due to the strong model potential between e-Ne and between e-Ar. Note that the model potential adopted supports unphysical bound states in each system. In reality, such bound states are not allowed since they are already occupied by core electrons. Thus we caution that the calculated results for NeH$^-$ and ArH$^-$ may be more questionable. On the other hand, full quantum chemistry calculations including all the electrons for these two systems may be difficult to reach the precision needed for spectroscopy. In view of the lack of any predictions on these two systems, we chose to present the results from this model calculation to guide future experimental search and to stimulate further work.

TABLE III. Calculated binding energies for ArH$^-$ and NeH$^-$ anions. The binding energies are given in cm^{-1}.

ArH$^-$		NeH$^-$	
$J=0$	$J=1$	$J=0$	$J=1$
−0.1084	−0.01598	−1.128	−0.7022
−2.470	−2.107	−15.55	−14.02
−13.95	−13.12	−75.91	−73.07
−49.04	−47.60	−206.0	−202.0
−124.2	−122.2	−415.2	−410.2
−248.5	−245.9	−712.3	−706.3
−426.1	−423.0		
−659.2	−655.6		
−948.9	−944.8		
−1295	−1290		

From these potential curves we calculated the binding energies for ^{20}NeH$^-$ and ^{40}ArH$^-$ anions. In Table III we present all the eigenenergies for $J=0$ and $J=1$ states. For higher J up to $J=14$, there exists at least one bound state for ^{20}NeH$^-$ and for J up to $J=24$ there exists at least one bound state for ^{40}ArH$^-$. The energies of these higher J states can be obtained from the authors directly. We note that the energy levels are of the order of hundreds of cm^{-1} for the lower states. Determination of the spectroscopy of these anions will be an area of experimental challenge.

III. SUMMARY

In this paper we calculated the binding energies of several weakly bound diatomic anions. Compared to the weakly bound van der Waals molecules which are electrically neutral, the weakly bound molecular ions may be easier to detect experimentally. For HeH$^-$ we found two bound states despite the fact that the van der Waals molecule HeH has no stable bound states. For the heavier NeH$^-$ and ArH$^-$ anions, we found a few bound states with binding energies in the order of a few hundreds of cm^{-1}. These molecular states are rather diffuse and it would be interesting to look for them experimentally. It would also be interesting to speculate whether these ions play any role in the cold interstellar molecular clouds, in particular, the two bound states in HeH$^-$, since both H and He are the most abundant elements in the universe. In the meanwhile we have searched for the possible existence of He$_2{}^-$ anions but our calculations showed that they do not exist.

ACKNOWLEDGMENTS

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