Three particle description of $H$-inert gas interaction

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We have analyzed the $H$-inert gas atom pair as a three particle system, an electron, a proton, and an inert gas atom. The interaction of the electron and the proton with the inert gas atom is described by a model potential with polarizability and nonadiabatic terms. This potential allows us to obtain reliable values for the energies at different separations, in particular dissociation energy at equilibrium separation. It also provides an alternate approach to the usual two body analysis in terms of van der Waals type of potential, and an insight into the physical structure of the system. © 2000 American Institute of Physics.

I. INTRODUCTION

The $H$-inert gas atom pair is an interesting example of an interaction between two atoms. It has been analyzed in terms of the perturbation arising from the interaction between the two atoms. This leads to the asymptotic van der Waals potential with various corrections incorporated to make it reliable over a wider range of separations between the two atoms. There is one aspect of the system which deserves a special consideration, that one of the two atoms, i.e., the hydrogen atom, is made up of only two particles, one electron, and one proton. It is therefore interesting to analyze the combined system in terms of three particles, an electron, a proton, and the inert gas atom, and obtain its wave function and energies. It may be noted that an electron in the presence of two cores has been described in terms of polarization potentials for several systems. However, in a neutral molecule, there is a cancellation of the leading terms and the system requires a more detailed treatment. Here, we consider the $H$-inert gas atom system in the Born–Oppenheimer approximation, with the electron moving in the potential of the proton and the inert gas atom. The complicated structure of the inert gas atom is incorporated in terms of an effective, model potential. We use this potential to develop a simple wave function for the ground state of the system, and calculate the energies for different separations of the proton and the inert gas atom. Apart from giving a useful expression for the wave function of the electron and reliable values for the energies, this approach provides an insight into the relation between the van der Waals potential description for the combined system and the polarizability potential description in terms of the electron, and the proton. Unless stated otherwise, we will use atomic units, $e=m_e=h=1$.

II. MODEL POTENTIAL FOR ELECTRON–INERT GAS ATOM INTERACTION

For developing the model potential for the electron–inert gas atom interaction, we first consider the more general case of the electron interacting with a closed shell core of charge $q_c$ and polarizability $\alpha_c$. We develop a simple potential which has the correct asymptotic behavior and an appropriate short-range structure. It is adjusted so as to give the correct valence electron energy in the alkali isoelectronic sequence, for the ground state. The potential for the electron–inert gas atom interaction is then obtained by extrapolation to the core charge $q_c \rightarrow 0$ corresponding to the inert gas atom.

Consider an electron at a large distance $r$ from a closed shell core of charge $q_c$. The potential for the interaction of the electron is

$$V = -\frac{q_c}{r} + \sum_i \left( \frac{1}{|r-r_i|} - \frac{1}{r} \right),$$

where the summation is over the electrons in the core. For large $r$ which may correspond to either the electron being in a highly excited state, or being bound in another atom, the leading term in the interaction potential is the Coulombic term with the net core charge $q_c$.

$$V^{(1)} = -\frac{q_c}{r}. \quad (2.2)$$

The contribution of the second term in Eq. (2.1) is incorporated perturbatively, using an unperturbed wave function which is a product of the core and electron energy eigenfunctions. The first order energy shift is small and may be neglected but the second order energy shift is important and gives rise to an induced polarizability term. To deduce this term, we note that the major contribution comes from the region $r > r_i$ and expand the potential in terms of Legendre polynomials, keeping only the leading $l = 1$ term. This gives rise to a second order energy shift,

$$\delta E^{(2)} = \sum_{i,k} \frac{|\langle 0,0 | r \cdot r_i/r^3 | j,k \rangle|^2}{E^{(c)}_i + E^{(n)}_0 - E^{(e)}_j - E^{(c)}_k}, \quad (2.3)$$

where $E^{(c)}_i$ and $E^{(e)}_j$ represent the core and electron energies, and for simplicity we have left out the summation over $l$. If we neglect the difference in the energies of the outer electron, we get the usual polarizability term which we separate out and write the energy shift as...
\[
\delta E^{(2)} = -\frac{1}{2} \alpha_c \langle 0 \mid \frac{1}{r^2} \mid 0 \rangle 
+ \sum_{j,k} \frac{(E_k^{(e)} - E_k^{(c)}) \langle 0,0 \mid \mathbf{r} \cdot \mathbf{r}_j / r^3 \mid j,k \rangle^2}{(E_0^{(e)} + E_0^{(c)} - E_j^{(c)} - E_k^{(c)}) (E_j^{(c)} - E_k^{(c)})},
\]

(2.4)

where \( \alpha_c \) is the dipolar polarizability of the core. The first term may effectively be regarded as corresponding to a polarizability potential term,

\[ V^{(2)}_{\text{pol}} = -\frac{\alpha_c}{2 r^2}. \]

(2.5)

The second term in Eq. (2.4), usually called the nonadiabatic term\(^2\) (nonadiabatic because it corresponds to the energy of the electron in the intermediate state being different from its energy in the unperturbed state), is small if the electron is loosely bound for which the \( E_k^{(e)} - E_0^{(e)} \) is small. We can estimate this term by substituting the first energy factor in the denominator of the expression in Eq. (2.4). This is similar to the expression used for the analysis\(^3\) of Rydberg energies\(^4\) and from accurate calculations.\(^5\) The single core energies, and there is a significant cancellation between this term and the quadrupolar term. One has accurate values for the dipolar polarizabilities of the core deduced from Rydberg energies\(^4\) and from accurate calculations.\(^5\) The single parameter \( R_c \) is determined by requiring that the ground state energy of this potential is equal to the experimental value of the valence electron energy. The input values of the valence electron energy, dipolar polarizabilities of the core, and the deduced values of the core radius \( R_c \) are given in Table I.

![Table I](https://example.com/table.png)

The model potential for the interaction of an electron with an inert gas atom is deduced from an extrapolation of the expression in Eq. (2.8). Since \( q_c = 0 \) in this case, we have

\[ V(r) = -\frac{\alpha_c}{2 (r^2 + R_c^2)^2} \text{ for } r > R_c \]

\[ = \infty \text{ for } r < R_c, \]

(2.9)

where \( \alpha_c \) is the dipolar polarizability of the inert gas atom. The value of \( R_c \) is taken from linear extrapolation of the values of \( R_c \) for cores with charges \( q_c = 1, 2 \) to the core with \( q_c = 0 \):

\[ R_c \text{(atom)} = 2R_c(q_c = 1) - R_c(q_c = 2). \]

(2.10)

We now use the potential in Eq. (2.9) to develop the potential for an electron and a proton interacting with an inert gas atom.

### III. POTENTIAL FOR ELECTRON–PROTON–INERT GAS ATOM INTERACTION

Consider an \( H \)-inert gas atom pair, in terms of an electron, proton, and an inert gas atom. We will discuss the system in terms of the Born–Oppenheimer approximation. Let the separation between the proton and the inert gas atom be \( R \), and let the distances of the electron from the proton and the inert gas atom be \( r_1 \) and \( r_2 \), respectively. Then based on the adiabatic electron–inert gas atom potential in Eq. (2.9), we propose a potential for the \( e^-p^- \)-inert gas atom

\[ V = \frac{1}{r_1} \frac{\alpha_c}{2 (r_1^2 + R_c^2)^2} + \frac{\alpha_c}{2 (r_2^2 + R_c^2)^2} + \frac{\alpha_c \cos \theta_2}{(r_2^2 + R_c^2)(R_1^2 + R_c^2)} \]

\[ + \frac{3 \alpha_c}{2 E} \frac{1}{(r_2^2 + R_c^2)^3} \text{ for } r_2, \ R > R_c \]

\[ = \infty \text{ for } r_2 \text{ or } R < R_c, \]

(3.1)

where

\[ V = \frac{\alpha_c}{2 (r^2 + R_c^2)^2} \]

\[ = \infty \text{ for } r < R_c, \]

(3.2)

\[ V = \frac{\alpha_c}{2 (r^2 + R_c^2)^2} \]

\[ = \infty \text{ for } r < R_c, \]

(3.3)

\[ V = \frac{\alpha_c}{2 (r^2 + R_c^2)^2} \]

\[ = \infty \text{ for } r < R_c. \]

(3.4)

\[ V = \frac{\alpha_c}{2 (r^2 + R_c^2)^2} \]

\[ = \infty \text{ for } r < R_c. \]

(3.5)
with $\theta_2$ being the angle between $r_2$ and $R$. In the expression in Eq. (3.1), the first term is the Coulombic interaction between the electron and the proton, and the second and the third terms are the polarizability terms of the type given in Eq. (2.9), for the electron and the proton interacting with the inert gas atom. The fourth term is effectively the interaction of the electron with the dipole moment induced in the inert gas atom by the proton and vice versa. The last term in Eq. (3.1) is the nonadiabatic term obtained in Eq. (2.7) with

$$E = \tilde{E}^{(c)} + \tilde{E}^{(e)}.$$  

It is important to observe that we did not include this nonadiabatic term in the discussion of the potential in Eq. (2.8) for alkali atom isoelectronic sequences since the energies of the valence electron are small compared with the energies of the electrons in the core. However, in the present case the electron is primarily bound to the proton and its energies are comparable to the energies of the outer electrons in the inert gas atom. Such a nonadiabatic term is not there in the Born–Oppenheimer approximation for the proton interacting with the inert gas atom. It should also be noted that we have not included the quadrupolar terms each of which has $1/r^6$ behavior, but because of the cancellation of the contributions from the electron and the proton terms, together go as $1/r^6$ for large separations, and therefore are less important than the $1/r^6$ terms.

It is very instructive to compare the potential in Eq. (3.1) with the van der Waals potential in terms of dispersion coefficients. To do this we express the potential in terms of $r_1$ and $\theta_1$ where $\theta_1$ is the angle between $r_1$ and $R$, and expand the potential in inverse powers of $R$. The leading $1/R^6$ terms cancel out, and on taking the expectation value between the ground state wave function of the hydrogen atom, we get for the effective two-body potential,

$$V(R) \to -\alpha_c \langle r_1^2 \rangle \frac{1}{R^6} + \frac{3 \alpha_c}{2 \tilde{E}} \frac{1}{R^6}$$  

for large $R$.  

For comparison with the van der Waals potential, we have for the leading dispersion term

$$V(R) = \frac{6}{R^6} \sum_{j,k} \frac{|\langle 0|r_1 P_1(\cos \theta_1)|j\rangle|^2 |\langle 0|r_1 P_1(\cos \theta_1)|k\rangle|^2}{E_0^{(c)} + E_0^{(e)} - E_j^{(c)} - E_k^{(e)}}$$

$$= -\frac{C_0}{R^6}.$$  

We carry out the adiabatic expansion for the electron energies in powers of $E_0^{(c)} - E_j^{(c)}$ relative to $E_0^{(e)} - E_j^{(e)}$, and get for the first term

$$V^{(1)} = \frac{6}{R^6} \langle r_1^2 \cos^2 \theta_1 \rangle \langle 0 \rangle \sum_j \frac{|\langle 0|r_1 \cos \theta_1|j\rangle|^2}{E_0^{(c)} - E_j^{(c)}}$$

$$= -\alpha_c \frac{\langle r_1^2 \rangle}{R^6},$$  

which is precisely the same as the first term in Eq. (3.4). The nonadiabatic corrections are of the same form as the expression in Eq. (2.7). We therefore take the coefficient of the nonadiabatic term in Eq. (3.4) to have the value which leads to the correct leading term in the dispersion potential,

$$\frac{3\alpha_c}{2\tilde{E}} = 3\alpha_c - C_6,$$  

where we have taken $\langle r_1^2 \rangle = 3$ for the hydrogen atom. The effective potential experienced by the electron in the presence of the proton and the inert gas atom is then given by the expression in Eq. (3.1) with the coefficient for the nonadiabatic term given by Eq. (3.7). One has accurate values for the dispersion coefficients. The main advantage of the present approach is that we can now obtain the wave function of the electron and the effects of overlap and exchange are incorporated in the effective potential.

**IV. WAVE FUNCTION FOR THE ELECTRON–PROTON–INERT GAS ATOM**

We now proceed to use the potential in Eq. (3.1) with the nonadiabatic coefficient given in terms of the dispersion coefficient $C_6$ in Eq. (3.7), to develop the wave function and calculate the energy for the ground state of $e - p$–inert gas atom.

Since the hydrogenic wave function is not affected significantly near the proton, and one has an infinite barrier at $r_2 = R$, near the inert gas atom, we consider a wave function of the form

<table>
<thead>
<tr>
<th>( H )</th>
<th>( Ne )</th>
<th>( Ar )</th>
<th>( Kr )</th>
<th>( Xe )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_v )</td>
<td>2.81</td>
<td>5.71</td>
<td>20.2</td>
<td>29.4</td>
</tr>
<tr>
<td>( R_a ) (a.u.)</td>
<td>6.0</td>
<td>6.1</td>
<td>6.3</td>
<td>6.4</td>
</tr>
<tr>
<td>( R_a ) (others)</td>
<td>(7.05) ( C_p )</td>
<td>(5.97) ( C_p )</td>
<td>(6.72) ( b )</td>
<td>(6.89) ( b )</td>
</tr>
<tr>
<td>( D ) (meV)</td>
<td>0.460</td>
<td>1.754</td>
<td>4.316</td>
<td>5.826</td>
</tr>
<tr>
<td>( D ) (others)</td>
<td>(0.46) ( C_p )</td>
<td>(1.90) ( C_p )</td>
<td>(4.67) ( b )</td>
<td>(5.82) ( b )</td>
</tr>
<tr>
<td>( E ) (5.0)</td>
<td>(b)</td>
<td>8.43</td>
<td>3.50</td>
<td>17.2</td>
</tr>
<tr>
<td>( E ) (5.5)</td>
<td>(b)</td>
<td>2.11</td>
<td>-0.891</td>
<td>0.546</td>
</tr>
<tr>
<td>( E ) (6.0)</td>
<td>(b)</td>
<td>0.108</td>
<td>-1.747</td>
<td>-3.872</td>
</tr>
<tr>
<td>( E ) (6.5)</td>
<td>(b)</td>
<td>-0.407</td>
<td>-1.575</td>
<td>-4.226</td>
</tr>
<tr>
<td>( E ) (7.0)</td>
<td>(b)</td>
<td>-0.451</td>
<td>-1.202</td>
<td>-3.484</td>
</tr>
<tr>
<td>( E ) (7.5)</td>
<td>(b)</td>
<td>-0.372</td>
<td>-0.866</td>
<td>-2.624</td>
</tr>
<tr>
<td>( E ) (8.0)</td>
<td>(b)</td>
<td>-0.280</td>
<td>-0.613</td>
<td>-1.912</td>
</tr>
</tbody>
</table>
\[ \psi = Ac^{-r_1}[1 - e^{-b(r_2 - R_c)}] \quad \text{for } r_2 > R_c \]
\[ = 0 \quad \text{for } r_2 < R_c \]

(4.1)

with \( b \) as a variational parameter. The calculations are carried out conveniently in terms of elliptic coordinates,

\[ u = \frac{r_1 + r_2}{R}, \quad v = \frac{r_1 - r_2}{R}, \]

(4.2)

\[ \nabla^2 = \left( \frac{2}{R} \right)^2 \frac{1}{u^2 - v^2} \left[ \frac{d}{du} (u^2 - 1) \frac{d}{du} + \frac{d}{dv} (1 - v^2) \frac{d}{dv} \right]. \]

(4.3)

\[ dV = 2\pi \left( \frac{R}{2} \right)^3 (u^2 - v^2) du dv, \]

(4.4)

where we have left out the \( \phi \) dependent terms. The results for the equilibrium separation of the nuclei and the corresponding dissociation energy, and energies at some other separations, along with the values of the variational parameter \( b \) are given in Table II.

V. RESULTS

The calculated values of the dissociation energies at equilibrium separation, are generally in good agreement with the experimental and earlier calculations.6–8 Our equilibrium separations are somewhat smaller than the earlier results6 for Kr and Xe but quite satisfactory for others. Their accuracy could be improved by including higher order polarizability terms. However, the main point of our analysis is that one can consider the \( H \)-inert gas interaction in terms of a three particle system, an electron moving in the potential of the proton and the inert gas atom. This approach in terms of the polarizabilities and nonadiabatic effects provides an alternate approach to the van der Waals type of potentials, and an insight into the physical structure of the system and the perturbed wave function of the electron in the \( H \) atom.