

Energy of immersing a He, Ne, or Ar atom or H₂ molecule into a low-density electron gas

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We calculate the energy $E(n)$ required to immerse a noble-gas atom or H₂ molecule into a low-density electron gas. The basic idea of Puska, Nieminen, and Manninen [Phys. Rev. B **24**, 3037 (1981)] is modified by replacing the scattering length a with an effective length \tilde{a} calculated by omitting polarization. The results are in good agreement with both *ab initio* and semiempirical results obtained by other methods.

I. INTRODUCTION

In recent years, the effective-medium theory has proved valuable for calculating interaction energies relevant to a wide variety of physical problems.¹⁻⁵ A fundamental quantity in this method is the energy $E(n)$ required to insert an atom into a *uniform* electron gas of density n , accompanied by a compensating positive background. This paper addresses the special case of a noble-gas atom or H₂ molecule inserted into a very-low-density electron gas. It will be seen possible then to make a very simple prediction for the coefficient α in the low-density expansion

$$E \rightarrow \alpha n, \quad n \rightarrow 0. \quad (1)$$

In this work we present an expression [Eq. (9)] for α in terms of quantities which have been calculated or measured previously. The resulting value can then be compared with others. One such result, which we call $\alpha^{(p)}$, was obtained by Puska, Nieminen, and Manninen⁶ (PNN, henceforth) using a method very similar to ours.

In practice, the limitation to low density may not be very restrictive because the regime of linear dependence of E on n is quite extended for noble-gas atoms.^{2,6} For example, the expression (1) should suffice in the regime $n < 10^{-4}$ a.u. relevant to physisorption interactions,^{3,5,7} i.e., for atomic positions beyond the classical turning point of atoms at thermal energy.

II. CALCULATION OF IMMERSION ENERGY

The PNN calculation incorporates two ingredients, one of which we adopt. This is their analysis of the interaction between the atom of interest and the rigid, positive jellium background. The latter interacts directly with the electrostatic field of the atom $\phi_a(r) > 0$.⁸ In the low- n limit, this field is unaffected by the environment, to lowest order. Thus, this interaction energy is

$$E_+ \rightarrow n\alpha_+, \quad (2)$$

$$\alpha_+ = \int \phi_a(\vec{r}) d\vec{r}. \quad (3)$$

The other interaction E_- , between the atom and the electron sea, can be evaluated on the basis of the independent electron model. For this, PNN used the expression derived by Fermi⁹ for the optical potential of an electron moving through a gas of scatterers,

$$E_- \rightarrow \alpha_-, \quad (4)$$

$$\alpha_-^{(p)} = 2\pi a. \quad (5)$$

In this expression, we have used atomic units (a.u.) and a is the electron-atom scattering length, known from gas-phase data.^{10,11} Combining these relations,

$$\alpha = \alpha_+ + \alpha_-, \quad (6)$$

$$\alpha^{(p)} = 2\pi a + \int \phi_a(\vec{r}) d\vec{r}. \quad (7)$$

PNN were able to assess this relation by comparing its predictions with those of their own independent, *ab initio* calculation of α , using density-functional methods. The test was made by evaluating a from Eq. (7) and comparing with experimental values. The results were rather disappointing, especially in the case of Ar. There, Eq. (7) yielded $a = 1.5$ a.u. while scattering experiments¹⁰ yield $a \simeq -1.5$ a.u.

We explain the discrepancy as follows. Equation (5) is *not* a correct measure of the atom-induced energy shift of the electron sea. Instead, a should be replaced by an "effective" scattering length \tilde{a} , i.e., we propose

$$\alpha_- = 2\pi\tilde{a}, \quad (8)$$

$$\alpha = 2\pi\tilde{a} + \int \phi_a(\vec{r}) d\vec{r}, \quad (9)$$

as substitutes for Eqs. (5) and (7). The quantity \tilde{a} is an otherwise unmeasurable parameter calculated by omitting atomic polarization from the theory of electron-atom scattering.¹¹⁻¹³ The reason for excluding this one-

TABLE I. Values of the electron-atom scattering length a and the "polarization-free" effective scattering length \bar{a} discussed in the text (lengths in a.u. = 0.529 Å).

System	\bar{a}	a
He	1.34 ^a	1.19 ^d
Ne	1.05 ^b	0.21 ^d
Ar	1.5 ^b	-1.55±0.15 ^e
H ₂	2.1 ^c	1.6 ^c

^aValue taken from average of Ref. 15, Fig. 1 and Ref. 11, Fig. 101 (based on calculations published in Ref. 14).

^bFrom Ref. 16.

^cFrom Ref. 17.

^dFrom Ref. 18.

^eFrom Ref. 10.

electron polarization from our problem is that it plays no role in the energetics of embedding an atom in an *isotropic* electron gas.

Fortunately, calculations of \bar{a} exist for the cases of H₂, He, Ne, and Ar.^{11,14-17} The computed values are shown in Table I along with values of a . The characteristic behavior, $\bar{a} > a$, is due to the fact that the exchange repulsion manifested in \bar{a} is reduced to a lesser (He) or greater (Ar) extent by the attractive polarization interaction, which is proportional to the polarizability of the atom.

We may now test our Eq. (9). To accomplish this we need to evaluate the integrated electrostatic potential of the atom. An integration by parts yields

$$\alpha_+ = \int \phi_a(\vec{r}) d\vec{r} = \frac{2\pi}{3} Z \langle r^2 \rangle, \quad (10a)$$

$$Z \langle r^2 \rangle = \int d\vec{r} r^2 n_a(r), \quad (10b)$$

where n_a is the density of the electrons in the free atom. Equation (10b) may then be evaluated from Pauli's relation¹⁹ for the diamagnetic susceptibility χ of the atom:²⁰

$$\chi = \frac{e^2 Z \langle r^2 \rangle}{6mc^2}. \quad (11)$$

Table II presents the quantities $\langle r^2 \rangle$, α_+ , α_- , and their sum, Eq. (9). Also shown are *ab initio* calculations of α by various workers.^{2,5-7} It is seen that there is overall consistency between these results and ours. Note that no free parameters have been used in our calculations.

The contrasting PNN model, Eq. (7), always predicts a smaller value of α than ours since $a < \bar{a}$. The predicted values, $\alpha(p) = 328, 520,$ and $1140 a_0^3$ eV for He, Ne, and Ar, respectively, are satisfactory only in the He case.

In making these evaluations it is important to use accurate values of $\langle r^2 \rangle$. In the case of Ne, for example, the experimental result shown in Table II is about 10% smaller than the result of either Hartree-Fock or self-interaction corrected local-spin-density (LSD) calculations.^{21,22} In this connection, we note that PNN blamed the LSD for the discrepancy in their calculations; however, their claim that a better theory would yield a larger value of $\langle r^2 \rangle$ runs counter to fact for both Ne and Ar.²³ In reality, correlation effects compress the electron cloud to a degree greater than the LSD predicts.²²

III. DISCUSSION

We have proposed a simple expression, Eq. (9), for calculating the proportionality factor relating the low-density immersion energy to n . Our results for α are in quite good agreement with other workers' *ab initio* calculations.

The ultimate check on the reliability of these predictions is experiment. Potentially the most sensitive test can be made with a comparison between adsorption and scattering data for these atoms on various surfaces. Necessarily, one must make assumptions or extensions of the theory to treat both van der Waals forces and the nonuniform density of the solid.^{5,7,24,25} These represent obstacles which may, we hope, be overcome before long.

Finally, we add a caveat concerning the relevance of this work to the case of an *ultralow*-density medium. In particular, it is clear that polarization *does* enter the extreme case of totally isolated and independent electrons

TABLE II. Parameters relevant to the immersion energy. The mean-square electron radius $\langle r^2 \rangle$ is expressed in a.u. The α coefficients (in eV a_0^3) are α_+ , from Eqs. (10) and (11), α_- , from Eq. (8), and α , from Eq. (9).

System	$\langle r^2 \rangle^a$	α_+	α_-	α	
				(This work)	(Other work)
He	1.19	135	229	364	305, ^b 313, ^c 329, ^d 375, ^e
Ne	0.85	485	179	664	670 ^b
Ar	1.38	1410	256	1666	1740 ^b
H ₂	2.51	286	359	645	

^aCalculated from Eq. (11) using χ values from Ref. 20. The relation in a.u. is χ (in 10^{-6} cc/mole) = 1.792 $Z \langle r^2 \rangle$. For H₂, the error in Eq. (11) is only $\sim 2\%$. See W. Weltner, Jr., J. Chem. Phys. 28, 477 (1958).

^b*Ab initio* results of Ref. 6 [not to be confused with the predictions of Eq. (7), also from that paper; those results are stated in the text, below Eq. (11)].

^cFrom Ref. 2.

^d*Ab initio* results of Ref. 7.

^e*Ab initio* results of Ref. 5.

interacting with the atom. It is only at finite density that our proposed substitution of \bar{a} for a is appropriate. A rather different reason for excepting the ultralow-density case is that the Wigner solid appears in this limit, invalidating the assumptions leading to Eq. (4). Unfortunately, we do not know at this time the rigorous bounds on the regime of validity of our results.

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