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Influence of retardation on the vibrational wave function and binding energy of the helium dimer

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Because of the extremely small binding energy of the helium dimer, the nuclear wave function is delocalized over an extremely large range of separations. One might therefore expect the properties of this extraordinary species to be sensitive to the potential at very large internuclear distances, r , where relativistic corrections to the usual van der Waals interaction may be important. We have estimated the effect of retardation, which changes the r^{-6} dependence of the potential to r^{-7} in the limit of large r , and have found that the binding energy and expectation value $\langle r \rangle$ are indeed significantly affected by its inclusion.

I. INTRODUCTION

The long-standing question of whether a bound state of $^4\text{He}_2$ exists has recently been resolved in our laboratory by detection of this species in extreme pulsed expansions of He having translational temperatures < 1 mK.¹ The experimental results are consistent with the best current theoretical estimates, which give a potential minimum of -10.96 ± 0.02 K relative to the separated atoms, an equilibrium separation $r_e = 2.97$ Å, and a single bound state ($v=0, j=0$) having an energy E_0 of only about -0.001 K relative to the separated atoms. Potentials with these features have been obtained independently within the last few years from empirical fits to a wide variety of scattering data, transport properties, and virial coefficients,^{2,3} and from *ab initio* quantum calculations carried out by at least three different methods.^{4,5,6} The vibrational wave function extends over an extremely large range of internuclear separations r , making $^4\text{He}_2$ uniquely a "long-range molecule"^{7,8} even in its ground state. The binding energy is therefore sensitive to the interaction potential energy at extraordinarily large separations, raising the issue of whether the current theoretical descriptions are quantitatively accurate in this regime.

In fact, all the *ab initio* quantum calculations mentioned above were carried out in the Born–Oppenheimer approximation, and with neglect of relativistic effects.⁹ Liu and McLean have specifically argued that the effect of these approximations is probably small on the scale of their estimated computational error.⁴ Their calculations were confined to values of r in the vicinity of the well (< 7 Å). However, because of the long-range nature of the helium dimer (*vide infra*), the binding energy of this unique species is expected to be sensitive to the shape of the potential at extremely large separations, even though the absolute value of the interaction potential at such distances may be much smaller than the error limits on the well depth.

The empirical fits of Aziz and Slaman^{2,3} do not include any explicit approximations. However, the potential forms used by these workers all have the r^{-6} dependence corre-

sponding to the nonrelativistic dispersion interaction in the limit of large separations. This dependence arises in second-order quantum perturbation theory from the mutual interaction of the instantaneous fluctuating dipole in one atom with the dipole induced instantaneously in the other atom.¹⁰

It is the goal of this paper to estimate the influence of finite electric field propagation time (retardation) on the properties of helium dimer. Retardation modifies the dispersion interaction at long range by allowing for the fact that the instantaneous atomic dipole may change during the time required for the electric dipole field to be propagated to the other atom and back at the speed of light.¹¹ As first described in the classic 1948 work of Casimir and Polder,¹² the effect of retardation is to decrease the strength of attraction at long range by multiplying the nonrelativistic dispersion potential $-a_6/r^6$ by a function $f(r) \leq 1$ which is asymptotically proportional to $1/r$. Thus, the retarded potential has the dependence r^{-7} at large r . Although the Casimir–Polder result has been subsequently confirmed by a variety of theoretical approaches,^{13–19} experimental observation of the retardation effect for atomic-scale systems has been very difficult because of its small magnitude.^{20–24} In contrast, retardation has been shown to be an important effect in some macroscopic systems, such as the electric dipole–dipole interactions between colloidal particles.^{25,26}

Qualitatively, retardation narrows the potential well of a diatomic molecule and therefore raises the energy of all bound states, decreasing the binding energy. However, the retardation coefficient $f(r)$ for ground-state atoms scales with the ratio r/λ_0 , where λ_0 is the longest wavelength of the dipole transition.¹² This makes the effect of retardation extremely small for ordinary diatomic molecules having internuclear distances of a few Å and λ_0 values of a few thousand Å. Of all ground-state molecular systems, helium dimer probably represents the best case for retardation to have a significant effect on a measurable property, because of (1) the extremely long range of its vibrational wave function; (2) the relatively small value of λ_0 (584.3 Å); and (3) the large fractional effect which a small change in energy will have on the already extremely small binding energy.

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II. CALCULATION OF THE RETARDATION COEFFICIENT $f(r)$

The ground-state interatomic potential for $^4\text{He}_2$ represents a case where the Casimir–Polder formulation of the retardation effect can be applied directly and exactly. A numerically exact calculation of the retardation coefficient requires a double summation over all the electronically excited states of the two atoms connected by dipole transitions, and a knowledge of all the corresponding oscillator strengths or, alternatively, the frequency-dependent polarizability. In atomic units, the expressions we used for the numerical calculations were

$$f(r) = \frac{a_{\text{ret}}(r)}{a_{\text{ret}}(0)}, \quad (1)$$

where

$$a_{\text{ret}}(r) = \pi^{-1} \int_0^\infty du \beta^2(iu) e^{-2ur\alpha} [(ur\alpha)^4 + 2(ur\alpha)^3 + 5(ur\alpha)^2 + 6(ur\alpha) + 3] \quad (2)$$

and

$$a_{\text{ret}}(0) = 3\pi^{-1} \int_0^\infty du \beta^2(iu). \quad (3)$$

Here $\beta(iu)$ is the dynamic dipole polarizability of the He atom at imaginary frequencies, and α is the fine structure constant. Note that $a_{\text{ret}}(0)$ is equal to the dipole–dipole dispersion coefficient a_6 , and consequently Eq. (3) provides an alternative way to calculate this coefficient.^{16,27,28}

Our calculations were carried out with two different analytic approximations to $\beta(iu)$ based on values of the effective oscillator strengths and eigenfrequencies obtained, respectively, by Chan and Dalgarno²⁹ and by Koide *et al.*³⁰ The parameters reported by Koide *et al.* give values of $\beta(iu)$ which lie completely within the very tight rigorous bounds given by Glover and Weinhold,³¹ while those of Chan and Dalgarno lie within those bounds over most of the frequency range. The corresponding values of a_6 also lie within the bounded range. Thus, both analytic forms should be considered reliable.

The numerical integration of Eqs. (2) and (3) (with r as a parameter) were carried out by Gauss–Laguerre quadrature. A total of 60 weights and zeros yielded convergence of the corresponding binding energies to a fractional uncertainty of 8×10^{-6} .

The calculated retardation coefficient $f(r)$ is shown in Fig. 1. The results corresponding to the two different estimates of $\beta(iu)$ are the same within the width of the plotted line. For r up to 20 Å they differ by $< 10^{-4}$. Note that the scale over which the retardation correction is significant is hundreds of Å. At the potential minimum, $f(r) = 0.9997$.

III. He_2 POTENTIALS WITH AND WITHOUT RETARDATION

To evaluate the effect of retardation, we chose the LM2M2 analytic representation of the helium dimer potential from Aziz and Slaman.² This potential, hereafter

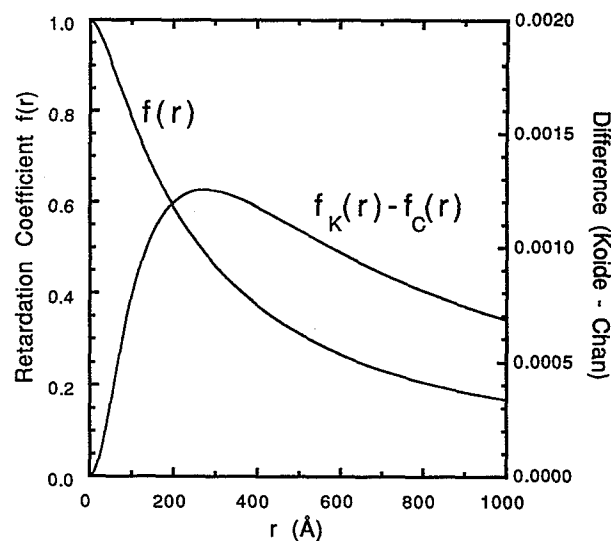


FIG. 1. Retardation coefficient $f(r)$ calculated numerically from Eq. (1). Also shown (right-hand scale) is the variation in $f(r)$ caused by slight differences in numerical parameters due to Koide *et al.* (Ref. 30) (f_K) and to Chan and Dalgarno (Ref. 29) (f_C).

referred to as $V(r)$, was constructed to fit the potential points calculated by Liu and McLean⁴ and Vos *et al.*⁵ within reasonable error limits, while also fitting the experimental viscosity and second virial coefficient data. It also reproduces the integral cross section data of Feltgen *et al.*³² and Kampe *et al.*,³³ and agrees with the new “exact” quantum Monte Carlo calculations of Anderson *et al.*⁶ within their error estimates.

The LM2M2 potential consists of an exponential repulsive term, plus attractive terms of the form $-a_6(r)/r^6 - a_8(r)/r^8 - a_{10}(r)/r^{10}$. All of the coefficients contain adjustable parameters, but the coefficients a_6 , a_8 , and a_{10} are all constant for separations larger than r_e . Retardation was introduced into the LM2M2 potential by simply multiplying the coefficient of the r^{-6} dipole–dipole dispersion term by $f(r)$ to give $-a_6(r)f(r)/r^6$. We denote the potential thus modified by LM2M2*, or $V^*(r)$.

It is appropriate to note here that the dipole–quadrupole and quadrupole–quadrupole terms (and indeed all higher-order contributions to the long-range potential) are also subject to retardation corrections. However, these terms make only tiny contributions to the helium dimer potential at distances where the retardation effect is large. For example, the r^{-8} term falls to a value $< 1\%$ of the r^{-6} term at a separation of 18 Å, where $f(r) = 0.98$.

Figure 2 shows the potential $V(r)$ and the difference $V^*(r) - V(r)$. At the scale shown for $V(r)$ (even magnified by a factor of 2000) the two potentials are indistinguishable within the width of the line. The difference potential is nowhere greater than 0.016 K, and the difference in the well depth is only 0.009 K—a value much smaller than any of the theoretical error estimates for $V(r)$. Nevertheless, the fractional contribution of retardation to the long range potential, as expressed by $f(r)$, is still large,

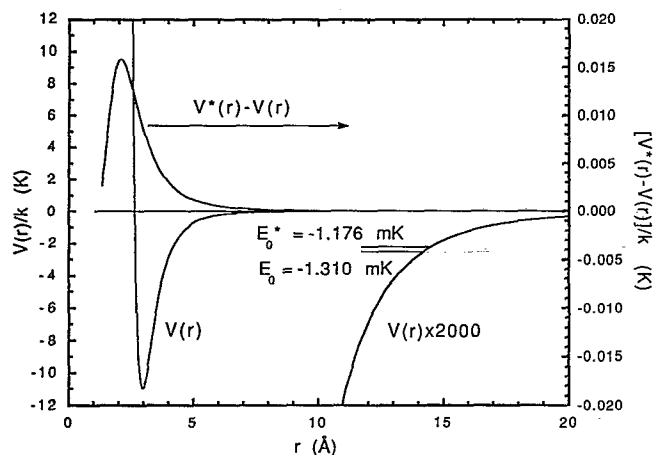


FIG. 2. The LM2M2 potential V and the difference potential $[V^* - V]$ as functions of internuclear separation r . The potentials are divided by the Boltzmann constant k and are thus expressed in units of K. Note the reduced scale for the difference potential.

and it is this long-range effect which is expected to be most significant.

IV. RESULTS

The radial wave functions and binding energies for the potentials $V(r)$ and $V^*(r)$ were calculated by the “shoot-ing method,”³⁴ with numerical integration carried out for distances between 2.5 and 2500 bohr to insure adequate convergence of the calculated properties. The wave functions, shown in Fig. 3, confirm the extremely long-range nature of ${}^4\text{He}_2$. Most of the probability distribution for r lies far into the classically forbidden region, and the probability remains significant even at separations >200 Å! The primary effect of retardation is to decrease the binding energy and thus extend the range of the interaction. This is consistent with effective range theory³⁵ for weakly bound systems, which gives a characteristic interaction length

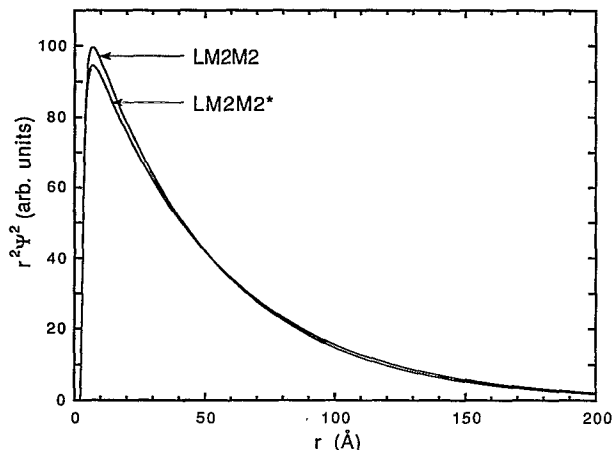


FIG. 3. Radial probability as a function of separation r for the unmodified LM2M2 potential and the LM2M2* potential modified to include retardation. The two distributions are normalized to the same integral, in arbitrary units.

TABLE I. Summary of helium dimer parameters estimated from the unmodified LM2M2 potential, and for the LM2M2* potential which is modified to include retardation.

Parameter	LM2M2	LM2M2*
V_{\min} (K)	-10.970	-10.961
r_e (Å)	2.9695	2.9695
E_0 (mK)	-1.310	-1.176
r_{\max} (class., Å)	14.09	14.32
ψ_{peak}^2 (Å)	3.77	3.77
$r^2\psi_{\text{peak}}^2$ (Å)	6.96	7.03
$\langle r \rangle$ (Å)	51.9	54.6

$$A = \hbar [2\mu |E_0|]^{-1/2}.$$

Table I lists the values of the well depth V_{\min} , the equilibrium separation r_e , the binding energy E_0 , the outer classical turning point for zero-point vibrational motion r_{\max} , the values of the separation at the maxima in ψ^2 and $r^2\psi^2$, and the expectation value of the radial coordinate, $\langle r \rangle$ for the unretarded and retarded potentials. The values listed for the retarded potential are independent of the method used to estimate $\beta_{\text{He}}(iu)$ to the indicated number of significant figures.

While the effect of retardation on the short-range properties of helium dimer are, as expected, quite small, retardation decreases the binding energy of this system by 10% and increases the expectation value of the internuclear separation by 5%. At $\langle r \rangle = 54.6$ Å, helium dimer is by a huge margin the largest of all ground-state diatomic molecules. The scattering length A for $V^*(r)$ is 101.5 Å, giving a low-energy limit to the scattering cross section of $\sigma_0 = 8\pi A^2 = 259\,000$ Å²!

As mentioned above, retardation influences the properties of the helium dimer principally through its effect on the shape of the potential at moderate to long range, not through a large absolute change in the interaction energy at any value of r . For example, at $r = \langle r \rangle = 54.6$ Å, the value of V is only -0.398 μK , and retardation decreases the value to $V^* = -0.358$ μK . Even though the largest absolute difference $[V^*(r) - V(r)]_{\max} = 0.016$ K occurs at $r < r_e$, the retardation influence in this region actually has only a small effect on the wave function and binding energy. If, for example, we remove the retardation correction entirely for $r < r_e$, but leave the long-range dependence of $V^*(r)$ unchanged, the retardation correction still makes a 9.1% correction to E_0 and yields a value of -1.191 K.

V. CONCLUSIONS

Quite apart from its small *absolute* effect on the interaction potential, retardation has a significant *fractional* effect on the binding energy and nuclear wave function of ${}^4\text{He}_2$, and therefore must be included for a quantitative description of this unique species. The experimental manifestation of this effect will probably most easily be detected by an $\sim 10\%$ increase in the low-energy ${}^4\text{He}-{}^4\text{He}$ scattering cross section or by a direct measurement of the ${}^4\text{He}_2$ binding energy, but any other measurable quantity which

is sensitive to the binding energy or long-range wave function will be similarly affected by retardation.

Note added in proof. A new measurement of the retardation effect on atom-wall interactions has appeared while the present manuscript was in press.³⁶

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