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Scattering lengths and effective ranges for He-He and spin-polarized H-H and D-D scattering

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The modifications of effective-range theory, necessitated by the long-range nature of interatomic dispersion and relativistic retardation forces, are discussed. A numerical comparison is given of parameters describing ^{3}He-^{3}He, ^{3}He-^{4}He, and ^{4}He-^{4}He scattering at very low energies calculated with several recently published interaction potentials. The effect of relativistic retardation on these parameters and on the calculated binding energies of the ^{4}He-^{4}He dimer is shown. It is demonstrated that all of these quantities are extremely sensitive to the potential. Scattering lengths and effective ranges for the lowest triplet interactions of H-H and D-D are also reported.

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Theoretical models for atomic collisions at very low energies are currently of interest because of the rapidly growing experimental field of ultralow temperature scattering measurements; such experiments contribute to the exploration of the bulk behavior of bosons in condensed matter. For example, a recent experiment [1] showed large cross sections in low-temperature ^{4}He-^{4}He elastic scattering. The large size of this cross section has its origin in a shallow well in the interaction potential which supports a weakly bound state (a dimer) near the continuum; the lighter isotopes ^{3}He are not bound. The binding energy is related to the low-energy cross sections and depends critically on the potential. Because the dimer is large, the binding is also altered by relativistic retardation [2,3]. A recent low-temperature experiment may be interpreted as providing direct evidence of the existence of helium dimers and of the effect of relativistic retardation [4].

The effective range expansion [5] must be modified for atom-atom collisions because the dispersion and retardation forces fall off with interatomic distance only as fast as inverse polynomials [6,7]. We present the modifications appropriate to our calculations below.

Calculation of the He-He interaction potential by semiempirical and *ab initio* methods currently attracts much interest and several recent versions are available [8–15]. Below we compare calculations of the parameters for low-energy collisions (scattering lengths and effective ranges) and of binding energies for some of these potentials and show that there remain fine details of the He-He interaction, other than retardation, to be determined before a definitive interpretation can be made of ultralow-temperature experimental data.

Recently there has been discussion of the calculation of s-wave scattering of spin-polarized hydrogen [16,17]. We give an evaluation of the scattering length and effective range that reduces, but not eliminates, uncertainties in the triplet interaction potential and we also present these values for deuterium scattering.

The first of the modern He-He interaction potentials was proposed by Aziz *et al.* [8]. It is a semiempirical potential of a Hartree-Fock dispersion form in which low-energy virial data sensitive to the attractive well are fitted. Later Aziz and Slaman [13] constructed an analytic expression for the *ab initio* potentials of Liu and McLean [9] and of Vos *et al.* [10], but found that it does not enable the virials and viscosity to be correctly predicted. By deepening the well within the error bounds of the Liu and McLean potential [9] and also introducing extra analytic flexibility into the upper attractive limb of the well (from about $5.6a_0$ to $8.0a_0$, where a_0 denotes the Bohr radius) they constructed a compromise analytic potential which mimics the *ab initio* calculations (except around $6a_0$–$7a_0$) and leads to calculated virials and room-temperature viscosity within experimental error. Recently a very accurate large-scale Monte Carlo calculation has been made by Anderson *et al.* [14]. The compromise potential of Aziz and Slaman is in good agreement with it and thus might be considered as the potential that is most consistent with the *ab initio* results and with the virial and transport data [13]. However, the *ab initio* calculation and this experimental data do not provide much information on the short-range repulsive wall. Nitz *et al.* [15] have discussed how small-angle scattering measurements in keV energy ranges [18] can be used to help evaluate the short-range interaction energies. Their recommended potential has the same attractive part as that of Aziz *et al.* [8], but differs at short range. We see below that this modification has a dramatic effect on ^{4}He-^{4}He scattering at ultralow temperatures.

The potentials we have used are those of Aziz *et al.*, 1987 [8], Aziz *et al.*, 1991 [13], Nitz *et al.* fitted to the 1987 potential of Aziz *et al.* [8,15], and Nitz *et al.* fitted to the 1991 potential of Aziz *et al.* [13,15]; we designate these in the tables by Aziz87, Aziz91, Nitz87, and Nitz91,

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respectively. The retardation was calculated from accurate polarizabilities [19].

The radial part $\frac{1}{r}y_l(r)$ of the lth partial wave describing scattering satisfies the differential equation

$$\frac{d^2y_l(r)}{dr^2}+\left[k^2-\frac{2\mu V(r)}{\hbar^2}-\frac{l(l+1)}{r^2}\right]y_l(r)=0, \tag{1}$$

where r is the internuclear distance, $k=\frac{\sqrt{2\mu E}}{\hbar}$ is the wave number in terms of the reduced mass μ and the energy of relative motion E, and $V(r)$ is the interaction potential. The boundary conditions are

$$y_l(0)=0 \tag{2}$$

and, as $r\to\infty$,

$$y_l(r)\to A_l[j_l(kr)+\tan\eta_l n_l(kr)]\ , \tag{3}$$

where A_l is an arbitrary normalization factor, $j_l(kr)$ and $n_l(kr)$ are the spherical Bessel and Neumann functions, respectively, and η_l is the phase shift to be determined.

At very small wave numbers the elastic scattering is dominated by s-wave scattering and, to a lesser extent, by p-wave scattering. For short-range potentials the s-wave phase shift satisfies the effective range expansion [5]

$$k\cot\eta_0=-\frac{1}{a}+\frac{1}{2}rk^2+O(k^4), \tag{4}$$

where a is the scattering length and r is the effective range. It has long been recognized that for the electron-atom and electron-ion polarization potentials, which fall off as r^{-4} as $r\to\infty$, Eq. (4) must be modified [6]. In the absence of relativistic retardation the potential $V(r)$ of Eq. (1) has, at large interatomic separations, a leading dependence $-c_6r^{-6}$, where c_6 is a dispersion coefficient; when retardation is considered, the leading term in the long-range potential is $-c_7r^{-7}$. Hinckelman and Spruch [7] have presented the modified effective range expansion for an r^{-6} potential which here becomes

$$\begin{aligned}k\cot\eta_0={}&-\frac{1}{a}+\frac{1}{2}rk^2-\frac{2}{15a^2}\pi\frac{\mu c_6}{\hbar^2}k^3\\&-\frac{8}{15a}\frac{\mu c_6}{\hbar^2}k^4\ln k+O(k^4).\end{aligned} \tag{5}$$

From Sec. II of Ref. [7] we find, for the retarded r^{-7} potential,

$$k\cot\eta_0=-\frac{1}{a}+\frac{1}{2}rk^2+\frac{4}{45a^2}\frac{\mu c_7}{\hbar^2}k^4\ln k+O(k^4). \tag{6}$$

The ranges of validity of the expansions (5) and (6) are much smaller in atom-atom scattering than in electron-atom scattering because the higher-order terms contain powers of the reduced mass which rapidly increase. However, the equations are applicable to cold collisions where k is small.

For the p wave we cannot make an effective range expansion for either r^{-6} or r^{-7} potentials [6]. However, we can still find the limiting value of $-k^{-3}\tan\eta_1$ for each of the two potentials from the expressions (69) and (70) given by Levy and Keller [20]. For the nonretarded potential we have

$$k^{-3}\tan\eta_1=-a_1+O(k)+O(k^2) \tag{7}$$

and for the retarded potential

$$k^{-3}\tan\eta_1=-a_1+O(k^2)+O(k^2\ln k). \tag{8}$$

Equations (7) and (8) enable us to evaluate the limiting values of $-k^{-3}\tan\eta_1$ for vanishing wave number k, where a_1 is the equivalent of the scattering length; the expressions for the coefficients of the powers of k and of the logarithmic term are complicated, but these terms can be eliminated by Richardson extrapolation, to zero k, of the calculated quantities $-k^{-3}\tan\eta_1$.

The binding energy E_b of a possible bound state with $l=0$ is related to the scattering length and effective range through Eqs. (5) and (6). Taking the binding energy as positive (so that the bound state lies at energy $-E_b$ relative to the energy at infinite separation) we define an imaginary wave number $-i\kappa$, at which the S matrix, considered as a function of k, is to vanish giving rise to a bound state [5], such that

$$\kappa=\frac{\sqrt{2\mu E_b}}{\hbar}. \tag{9}$$

We can substitute $k=-i\kappa$ into the first two terms of Eqs. (5) and (6); we cannot depend on the higher-order terms in their present forms because the analysis in Ref. [7] does not explicitly contain the analytic continuation from real to complex wave number, but the ^{4}He-^{4}He dimer is so weakly bound that higher-order terms are unimportant (κ is typically $0.01a_0^{-1}$ or smaller). For both equations we find

TABLE I. Scattering lengths and effective ranges (Å) for He-He.

Potential	Scattering length a			Effective range r		
	^{3}He-^{3}He	^{3}He-^{4}He	^{4}He-^{4}He	^{3}He-^{3}He	^{3}He-^{4}He	^{4}He-^{4}He
			Without retardation			
Aziz87 [8]	-7.30	-18.2	88.4	13.3	9.70	7.27
Aziz91 [13]	-7.15	-17.6	100.	13.5	9.79	7.32
Nitz87 [8,15]	-8.30	-23.8	46.1	12.5	9.14	6.90
Nitz91 [13,15]	-8.10	-22.6	49.7	12.6	9.23	6.96
			With retardation			
Aziz87 [8]	-7.23	-18.0	92.4	13.4	9.72	7.29
Aziz91 [13]	-7.09	-17.4	105.	13.5	9.81	7.34
Nitz87 [8,15]	-8.22	-23.4	47.1	12.5	9.16	6.92
Nitz91 [13,15]	-8.02	-22.3	50.9	12.6	9.25	6.97

TABLE II. Limiting value of $-k^{-3}\tan\eta_1$ as $k \rightarrow 0$ (Å^3) for He-He.

Potential	Without retardation			With retardation		
	^{3}He-^{3}He	^{3}He-^{4}He	^{4}He-^{4}He	^{3}He-^{3}He	^{3}He-^{4}He	^{4}He-^{4}He
Aziz87 [8]	-24.9	-30.9	-40.8	-24.7	-30.7	-40.5
Aziz91 [13]	-24.8	-30.8	-40.6	-24.6	-30.6	-40.3
Nitz87 [8,15]	-25.5	-31.9	-42.5	-25.3	-31.6	-42.2
Nitz91 [13,15]	-25.4	-31.7	-42.2	-25.2	-31.5	-41.9

$$\frac{1}{a} \approx \kappa - \frac{1}{2} r \kappa^2. \tag{10}$$

We solved Eq. (1) by Numerov's method for several small values of the wave number k and the potentials listed above and calculated the s-wave and p-wave phase shifts by fitting the numerical solutions asymptotically to the boundary conditions (3). We calculated the scattering lengths and effective ranges from Eqs. (5) and (6) by Richardson extrapolation for the s waves and the limiting values of $k^{-3}\tan\eta_1$ (for vanishing k) from Eqs. (7) and (8), also by Richardson extrapolation. The reduced masses used were $2748.9432 m_e$ for ^{3}He-^{3}He, $3135.3481 m_e$ for ^{3}He-^{4}He, and $3648.1498 m_e$ for ^{4}He-^{4}He, where m_e is the mass of an electron. The values of c_6 and c_7 used were $1.460\,978 a_0^6$ hartree and $479.8634 a_0^7$ hartree, respectively [19].

We show these calculations in Tables I and II where a considerable variation with potential is seen in the s-wave data. These data, except in ^{4}He-^{4}He collisions, are little affected by retardation; the choice of potential has a much greater influence. The ^{4}He-^{4}He scattering lengths are increased by up to 5% by retardation, but the choice of potential can alter them by a factor of up to 2; the effective ranges vary only slightly with retardation. The p-wave data exhibit less than 1% variation with retardation. They are also less influenced by the short-range modifications to the potential as is expected since a p wave penetrates to a lesser degree than an s wave.

The large scattering lengths for ^{4}He-^{4}He collisions contribute to the large cross sections measured by Mester *et al.* [1] and they reflect the presence of a weakly bound state near the edge of the continuum. We calculated the energies of this state for the various potentials by solving Eq. (1), but with the *eigenvalue* condition that its solution decay as $\exp(-\kappa r)$ for large r; using the secant method we adjusted the binding energies to match forward and trial backward solutions. The binding energies are shown in Table III. Again there is great variation with potential. The state is large in spatial extent and, because κ is small, it has considerable probability beyond the outer classical turning point. Hence it is a good candidate for reflecting the influence of retardation as has been noted by Luo *et al.* [3]; the present calculations demonstrate up to 10% reduction with retardation. The short-range modification proposed by Nitz *et al.* [15] has the effect of lowering the bound state into the well which reduces its extent; we see that the binding energies for those potentials modified at short range show only about 5% change with retardation. Overall, however, the choice of potential overwhelms the retardation effect. Our value agrees with that of Luo *et al.* for the 1991 potential of Aziz *et al.* [13]. Luo *et al.* determined the scattering length from the binding energy by using the first term of Eq. (10). We have calculated the binding energies from the scattering data from the same single term formula and also from both terms, which provides more precise values [21]. We show these values in Table III; the leading quadratic dependence of E_b on a, implied by Eqs. (9) and (10), shows why the binding energies are twice as sensitive to retardation as the scattering lengths. Our two term calculations agree with the direct evaluations of the binding energies.

It is clear from the results presented above that there remain uncertainties in the He-He interaction to which calculated low-temperature phenomena are extremely sensitive; they outweigh retardation corrections which are nonetheless important.

Recently Jamieson *et al.* [16] demonstrated that the calculated s-wave scattering length for hydrogen atom scattering through the $b\,^3\Sigma_u{}^+$ molecular state is ill-conditioned to small changes in the fitting of the potential at interatomic separations between $12a_0$, where the currently available *ab initio* data stops, and $15a_0$ where the long-range data starts. Tiesinga [17] has shown that if the energies of Frye *et al.* [22] are taken as being relative to the dissociation limit instead of being absolute values as was assumed by Jamieson *et al.*, then the long-range form, valid for interatomic distances greater than $15a_0$, matches the *ab initio* energy more closely at $12a_0$ and, while the ill-conditioning remains, the uncertainty in the calculated scattering length is considerably reduced. He estimated a residual uncertainty of $0.1a_0$.

We recalculated the s-wave scattering length and effective range with the adjusted *ab initio* potential of Frye *et al.* in which the (now small) difference between the long-range form and the desired smooth potential in the interval from $12a_0$ to $25a_0$ was interpolated by a smooth

TABLE III. Binding energies of ^{4}He-^{4}He (mK) without and with retardation.

	Direct		Eq. (10) (two terms)		Eq. (10) (one term)	
Potential	Without	With	Without	With	Without	With
Aziz87 [8]	1.693	1.544	1.69	1.54	1.55	1.42
Aziz91 [13]	1.310	1.176	1.31	1.18	1.21	1.09
Nitz87 [8,15]	6.760	6.437	6.76	6.44	5.70	5.45
Nitz91 [13,15]	5.745	5.447	5.75	5.45	4.91	4.67

piecewise continuous fit. The calculation was performed in the manner described above. Our scattering length of $1.212a_0$ agrees with $1.2\pm\ 0.2a_0$ of Tiesinga (the extra $0.1a_0$ uncertainty arising around the potential minimum).

A more recent calculation of the interaction in the triplet molecular state has been made by Kolos and Rychlewski [23]. It comprises an improved Born-Oppenheimer potential and an adiabatic correction arising from the relative kinetic energy of the nuclei, the kinetic energy of the electrons, and a mass polarization term. Unfortunately it is available only over the range from $1a_0$ to $8a_0$ although it does contribute more energy points in the vicinity of the left limb of the van der Waals minimum. However, the Born-Oppenheimer potential matches the shifted potential of Frye *et al.* around $7a_0$–$8a_0$, supporting their suggestion that their energies should be taken relative to the dissociation limit. The adiabatic corrections are small beyond $8.0a_0$. We constructed a potential consisting of the energies of Kolos and Rychlewski from $1a_0$ to $8a_0$ matched to the adjusted energies of Frye *et al.* and the long-range form as described in the preceding paragraph. A calculation of the scattering length with this new potential yielded a value of $1.224a_0$. We also examined the effect of retardation using the modified interaction calculated by Marinescu [24]. The results are shown in Table IV; the reduced masses used were $918.0758m_e$ for hydrogen and $1835.7415m_e$ for deuterium. The value of c_6 used was $6.4990a_0^6$ hartree [25]. The value of c_7 is $23\beta^2/4\pi\alpha$, where β is the static dipole polarizability and α is the fine structure constant [2]; the value taken was $1269.748a_0^7$ hartree.

TABLE IV. Scattering lengths and effective ranges (Å) for H-H and D-D.

	H-H	D-D
Scattering length a	0.648	-4.01
Effective range r	184.	35.5

The adiabatic corrections decreased the scattering length (algebraically) by about $\frac{1}{10}$% for each species. Retardation also has little effect; the magnitude of the scattering length for hydrogen is increased by about $\frac{3}{20}$% and for deuterium decreased by about $\frac{1}{10}$%. For deuterium Gutierrez *et al.* obtained −3.63 Å for the scattering length and 40.4 Å for the effective range with an older potential.

The remaining uncertainty in the hydrogen scattering length could be greatly reduced by accurate calculations of the interaction energies at interatomic separations out to at least $15a_0$ [16] with more energies being given around the potential minimum as suggested by Tiesinga [17].

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[1] J. C. Mester, E. S. Meyer, M. W. Reynolds, T. E. Huber, Z. Zhao, B. Freedman, K. Kim, and I. F. Silvera, Phys. Rev. Lett. **71**, 1343 (1993).
[2] H. B. G. Casimir and D. Polder, Phys. Rev. **73**, 360 (1948).
[3] F. Luo, G. Kim, G. C. McBane, C. F. Giese, and W. R. Gentry, J. Chem. Phys. **98**, 9687 (1993).
[4] F. Luo, G. C. McBane, G. Kim, C. F. Giese, and W. R. Gentry, J. Chem. Phys. **98**, 3564 (1993).
[5] J. M. Blatt and J. D. Jackson, Phys. Rev. **26**, 18 (1949).
[6] T. F. O'Malley, L. Spruch, and L. Rosenberg, J. Math. Phys. **2**, 491 (1961).
[7] O. Hinckelmann and L. Spruch, Phys. Rev. A **3**, 642 (1971).
[8] R. A. Aziz, F. R. W. McCourt, and C. C. K. Wong, Mol. Phys. **61**, 1487 (1987).
[9] B. Liu and A. D. McLean, J. Chem. Phys. **91**, 2348 (1989).
[10] R. J. Vos, J. H. van Lenthe, and F. B. van Duijneveldt, J. Chem. Phys. **93**, 643 (1990).
[11] R. A. Aziz and M. J. Slaman, Metrologica **27**, 211 (1990).
[12] R. A. Aziz, A. Krantz, and M. J. Slaman, Z. Phys. D **21**, 251 (1991).
[13] R. A. Aziz and M. J. Slaman, J. Chem. Phys. **94**, 8047 (1991).
[14] J. B. Anderson, C. A. Traynor, and B. M. Boghasian, J. Chem. Phys. **99**, 345 (1993).
[15] D. E. Nitz, D. Sieglaff, M. Lagus, E. Abraham, P. Wold, and K. Swanson, Phys. Rev. A **47**, 3861 (1993).
[16] M. J. Jamieson, A. Dalgarno, and J. N. Yukich, Phys. Rev. A **46**, 6956 (1992).
[17] E. Tiesinga, Phys. Rev. A **48**, 4801 (1993).
[18] J. H. Newman, K. A. Smith, R. F. Stebbings, and Y. S. Chen, J. Geophys. Res. **90**, 11 045 (1985); D. E. Nitz, R. S. Gao, L. K. Johnson, K. A. Smith, and R. F. Stebbings, Phys. Rev. A **35**, 4541 (1987).
[19] M. J. Jamieson, G. W. F. Drake, and A. Dalgarno, Phys. Rev. A (to be published).
[20] B. H. Levy and J. B. Keller, J. Math. Phys. **4**, 54 (1963).
[21] G. Gutierrez, M. de Llano, and W. C. Stwalley, Phys. Rev. B **29**, 5211 (1984).
[22] D. Frye, G. C. Lie, and E. Clementi, J. Chem. Phys. **91**, 2366 (1989).
[23] W. Kolos and J. Rychlewski, J. Mol. Spectrosc. **143**, 237 (1990).
[24] M. Marinescu (private communication).
[25] Y. M. Chan and A. Dalgarno, Molec. Phys. **14**, 101 (1968).