Evaluating the integrals J_l, one obtains $\tan\delta_l$, and then adjusts the various parameters to reproduce the phase shifts computed from the 6–12 and Yntema-Schneider potentials. The parameters which give the best fit to the phase-shift data are tabulated in Table II. The phase shift for the 6–12 potential[7] was available for 20 equally spaced momentum values between 0.086 and 1.564 Å^{-1} and for the Yntema-Schneider potential[29,2] for 25 momentum values between 0.086 and 1.954 Å^{-1}. The separable potentials were fitted to these values, and the

deviation quoted in Table II was computed by using

$$(\text{Dev})_l = \left\{ \frac{1}{N} \sum_{n=1}^{N} \left[(2l+1) \times (\delta_l^{\text{deB or Y-S}}(n) - \delta_l^{\text{Sep}}(n)) \right]^2 \right\}^{1/2}, \quad (A6)$$

where $N = 20$ or 25. The coupling constants for the repulsive core are taken as large, but finite, positive numbers of the order of 10^4 to 10^5 times the magnitude of the attractive coupling constants.

Binding in Helium Intermolecular Potentials

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A method of counting bound states is modified and applied to singular helium intermolecular potentials to determine the conditions under which such potentials support a single bound state. Results are presented for the "6-9" and "6-12" potentials and compared with the results of earlier variational calculations.

I. INTRODUCTION

THERE has been some discussion in the literature[1-3] as to the existence of bound states in the various intermolecular potentials proposed for helium.[4] This matter is important since the bound states enter into the calculation of virial coefficients and transport properties of helium.[3] The earlier calculations of Refs. 1 and 2 were based on variational methods for determining the values of the potential parameters just sufficient to bind a single s state; the results are of uncertain accuracy and bound the correct values from one side only. This situation is further aggravated by the fact that, with the intermolecular potentials generally used for helium, a bound state, if it exists, is bound very weakly.

In the present work we give some results for the critical potential parameters using a modification of a method for counting the bound states in central potentials,[5] the modification being required because of the highly singular potentials with which we must deal. This method characterizes the potential by a single parameter ω, such that increasing ω results in an everywhere-more-attractive potential. By direct in-

tegration of the zero-energy Schrödinger equation, one determines the inverse scattering length a^{-1} of the potential as a function of ω. The potential that will just bind a single state is then characterized by the critical value of ω, i.e., the smallest ω for which $a^{-1} = 0$. This method, with its modification as given below, is straightforward, applicable to a wide class of singular potentials, and not beset by the uncertainties associated with variational methods.

II. METHOD OF CALCULATION

The zero-energy reduced radial Schrödinger s-wave equation for a two-body system of reduced mass m interacting through a potential $V(r)$ is

$$-\frac{\hbar^2}{2m} \frac{d^2u}{dr^2} + V(r)u(r) = 0.$$

Standard intermolecular potentials have the Lennard-Jones form

$$V(r) = (\hbar^2/2ma_0^2)[\alpha(a_0/r)^n - \beta(a_0/r)^6]$$

with $a_0 = \hbar^2/me^2$, and α and β are dimensionless constants. The dominant features of this potential are (1) the attractive induced dipole-dipole interaction varying as $1/r^6$, and (2) the hard core which goes as $1/r^n$. The exponent n is generally chosen between 8 and 14. We shall deal here with the two cases $n = 9$ and $n = 12$ (commonly called the 6–9 and 6–12 potentials). To associate the parameter ω with the attractive term in

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[2] J. E. Kilpatrick and M. F. Kilpatrick, J. Chem. Phys. **19**, 930 (1951).

[3] A. Pais and G. E. Uhlenbeck, Phys. Rev. **116**, 250 (1959).

[4] J. O. Hirschfelder, C. F. Curtis, and R. B. Bird, *Molecular Theory of Gases* (John Wiley & Sons, Inc., New York, 1954).

[5] H. M. Schey and J. L. Schwartz, Phys. Rev. **139**, B1428 (1965). The reader should consult this reference for details of the calculational method.

$V(r)$, we set

$$r = \alpha^{1/(n-2)} a_0 x$$

and obtain

$$d^2u/dx^2 - W(x)u = 0$$

with

$$W(x) = 1/x^n - \omega/x^6$$

and

$$\omega = \beta/\alpha^{4/(n-2)}.$$

Unfortunately, it is not possible to apply immediately the method of Ref. 5, because of the extremely rapid variation of $W(x)$ at small x. Therefore we have adopted the following procedure. Noting that $W(x)$ intersects the x axis at $x_0 = (1/\omega)^{1/(n-6)}$ we define

$$x_\theta = \theta(1/\omega)^{1/(n-6)} = \theta x_0, \quad 0 \leq \theta \leq 1,$$

and the auxiliary potentials

$$W_H(\theta, x) = W(x_\theta), \quad x \leq x_\theta,$$
$$= W(x), \quad x \geq x_\theta,$$

and

$$W_V(\theta, x) = \infty, \quad x < x_\theta,$$
$$= W(x), \quad x \geq x_\theta.$$

For a decreasing sequence of values of θ starting with $\theta = 1$, we apply the method of Ref. 5 to find the critical values $\omega_H(\theta)$ and $\omega_V(\theta)$ for which $W_H(\theta, x)$ and $W_V(\theta, x)$ will each just support a single bound state. Since the potential $W_H(\theta, x)$ is everywhere at least as attractive as $W(x)$ which in turn is everywhere at least as attractive as $W_V(\theta, x)$ it is clear that if ω_c is the critical value associated with the actual potential $W(x)$, then

$$\omega_H(\theta) < \omega_c < \omega_V(\theta).$$

Further as $\theta \rightarrow 0$, $\omega_H(\theta)$ and $\omega_V(\theta)$ approach a common limit, which is the value of ω_c.[6]
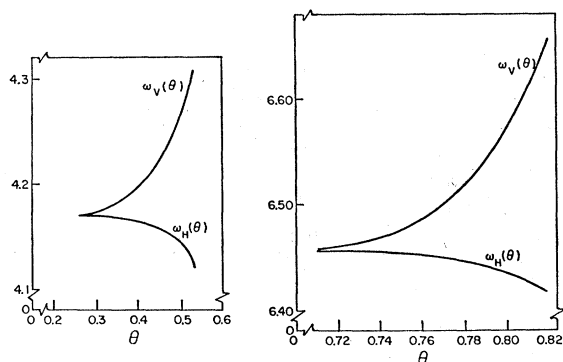

FIG. 1. (a) The critical values ω_H and ω_V as functions of θ for the 6–9 potential. (b) The critical values ω_H and ω_v as functions of θ for the 6–12 potential.

[6] The application of limiting procedures to singular potentials, i.e., the general peritization technique, is dubious when used in an exotic manner [see, e.g., F. Calogero, Phys. Rev. 139, B602 (1965)]. However, such reservations do not apply to the above procedure.

TABLE I. The critical value ω_c for the 6–9, 6–10, and 6–12 potentials.

	Present calculation	Kihara et al.[a]	Kilpatrick and Kilpatrick[b]
6–9	4.1700±0.0005	4.15	⋯
6–10	⋯	5.00	⋯
6–12	6.4565±0.0005	6.41	6.452

[a] See Ref. 1.
[b] See Ref. 2.

III. RESULTS AND DISCUSSION

We have applied the procedure outlined above to the potential $W(x)$ for $n = 9$ and $n = 12$. The results are shown in Fig. 1. The fact that the two curves for each potential are already close to one another for quite large values of θ is a direct consequence of the rapid climb of the potential in the region of small x. The zero-energy wave function is so strongly excluded from the vicinity of the origin that details of the potential there do not influence the wave function. Our calculated critical values as well as variational results reported by Kihara et al.[1] and Kilpatrick and Kilpatrick[2] are shown in Table I. The results of the present calculation agree well with the variational calculations reported in the past, although their accuracy is established here for the first time. The extraordinary success of the variational calculations is probably due to the existence of an almost everywhere analytic solution to the 6–10 potential.[1] This solution provided a good functional form for a trial wave function in the closely related 6–9 and 6–12 potentials since, as already observed, with such a strongly repulsive core the wave function is almost zero near the origin, and consequently all calculations tend to be insensitive to the detailed structure of the core. In fact the analytical form of the repulsive portion of the intermolecular potential is not well known and is generally chosen only as a matter of convenience.[7]

The currently accepted parameters of the helium-helium 6–12 interaction,[1] determined from the second and third virial coefficients, give a value of $\omega \approx 7.4$ and hence there is a single weakly bound s state.

[7] In addition, an exponential form of repulsion, cut off at extremely small distances, has been considered [see J. E. Kilpatrick, W. E. Keller, and E. F. Hammel, Phys. Rev. 97, 9 (1955)].