Three-Body Bound State in He⁴†

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The binding energy of three He⁴ atoms, subject to pair forces, is investigated numerically for a number of proposed intermolecular potentials and for a series of square wells. For some potentials a 3-body bound state is found, for others not. However, a direct correlation is found between 2-body and 3-body binding. The need for more accurate experimental data is discussed.

RECENTLY, in order to explain the low-temperature behavior of the third virial coefficient of helium 4, it has been proposed that helium atoms might form 3-body bound states.[1] The purpose of this note is to report on the result of an investigation of the binding energy of these triatomic molecules for a variety of 2-body potentials, using a modification of a variational program originally developed for the study of the triton.[2]

We have considered the following potentials:

(1) LJ1—A Lennard-Jones 12-6 potential with parameters ϵ and σ determined empirically by de Boer and Michels[3] by comparing quantum-mechanical expressions for the second virial coefficient with the experimental data at temperatures above 40°K. These parameters are then found[4,5] optimum for a fit of the data available up to 1955 from low temperatures (<2°K) up to 400°K.

$$V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6].$$

(2) MR5—A modified Mason-Rice (exp-6) potential proposed[6] by Kilpatrick, Keller, and Hammel after new experimental work by Keller[7] below 4.2°K. It is considered by them to be their best potential.

$$V(r) = \frac{\epsilon}{1 - 6/\alpha}\left[\frac{6}{\alpha}e^{\alpha(1-r/r_0)} - \left(\frac{r_0}{r}\right)^6\right].$$

(3) LJ3—A Lennard-Jones potential constructed along directions laid down in the paper of KKH[6] so as

to give essentially the same virials as the MR5. However, it has a very different shape.

(4) MR1—The original Mason-Rice[8] (exp-6) potential which fits high-temperature second virial data but not the low-temperature data.

(5) KMS—A 9-6 potential proposed by Kihara, Midzuno, and Shizume,[9] with constants determined from an analysis of the second and third virial coefficient above the Boyle temperature.

$$V(r) = \epsilon[2(r_0/r)^9 - 3(r_0/r)^6].$$

Of the above potentials, the first two have no 2-body bound states, the third has a very weak 2-body binding energy, and the latter two, substantially stronger potentials, have a discrete 2-body level.

In addition to these five potentials, we have investigated a series of square wells in an effort to clarify the role of the hard core and to establish the relationship between 2-body and 3-body binding energy.

(6) SQA—A series of hard cores with attached square wells. One of these is essentially the same potential used by Larsen[1] in his study of the third virial coefficient and was fitted to second virial-coefficient data under the constraint that there exists no 2-body bound state. The members of this series differ by systematic variation of the hard core radius, keeping the depth and the range of the attractive well constant.

$$V(r) = \infty, \quad r < \sigma$$
$$= -\epsilon, \quad \sigma < r < \sigma + r_0$$
$$= 0, \quad \sigma + r_0 < r.$$

(7) SQB—Starting from the same reference potential as in SQA, we have considered systematic increases in the well depth, keeping the core radius and square well range fixed.

The result of the calculations are found listed in Table I, together with an estimate of the strength parameter s (defined by requiring that the potential

¹ S. Larsen, Phys. Rev. **130**, 1426 (1963).
² G. Derrick, D. Mustard, and J. M. Blatt, Phys. Rev. Letters **6**, 69 (1961); J. M. Blatt, G. H. Derrick, and J. N. Lyness, *ibid.* **8**, 323 (1962).
³ J. deBoer and A. Michels, Physica **5**, 945 (1938).
⁴ J. deBoer and A. Michels, Physica **6**, 97 (1939).
⁵ J. E. Kilpatrick, W. E. Keller, E. F. Hammel, and N. Metropolis, Phys. Rev. **94**, 1103 (1954).
⁶ J. E. Kilpatrick, W. E. Keller, and E. F. Hammel, Phys. Rev. **97**, 9 (1955).
⁷ W. E. Keller, Phys. Rev. **97**, 1 (1955).
⁸ E. Mason and W. Rice, J. Chem. Phys. **22**, 522 (1954).
⁹ T. Kihara, Y. Midzuno, and T. Shizume, J. Phys. Soc. Japan **10**, 249 (1955).

TABLE I. Two-body and three-body binding energies.

Potential	σ (Å)	r_0 (Å)	α	ϵ/k (°K)	s	2-body binding energy (°K)	3-body binding energy (°K)
LJI	2.56	...	...	10.22	0.99	...	...
MR5	...	3.1894	12.4	7.5628	...	...	...
LJ3	2.556	...	...	10.46	1.01	...	...
MR1	...	3.135	12.4	9.16	1.16	0.034	≥ 0.25
KMS	...	3.11	...	7.82	1.15	...	≥ 0.264
SQA1	0.3	3.86124	...	2.0	0.997	...	≥ 0.267
SQA2	0.8	3.86124	...	2.0	0.997	...	≥ 0.135
SQA3	1.6	3.86124	...	2.0	0.997	...	≥ 0.05
SQA4	2.1	3.86124	...	2.0	0.997	...	$\geq 0.005^{a}$
SQB1	2.1	3.86714	...	2.0	1.00	...	...
SQB2	2.1	3.86714	...	2.1	1.05	0.0031	≥ 0.078
SQB3	2.1	3.86714	...	2.2	1.10	0.012	≥ 0.172
SQB4	2.1	3.86714	...	2.3	1.15	0.028	≥ 0.266

ᵃ This binding is of such low order as to be within the calculation error.

divided by s give zero 2-body binding), and the 2-body binding energy, if any.

In our trials of SQA, we have kept the 2-body binding energy fixed. We, therefore, expect that these results reflect mainly the effect on the 3-body binding of choosing different core radii. Although the results obtained for square wells do not carry over strictly to other potentials, calculations based on square wells place the results of the calculations of the other potentials in proper perspective and enable us to attain a semiquantitative understanding of their behavior.

We see that if we have a small core[10] then a potential exhibiting zero 2-body binding has a 3-body bound state. However, in the range of repulsive cores expected in actual molecular forces, such a potential yields 3-body binding of such low order as to be within the calculation error. *For repulsive cores of the right order of magnitude, our results indicate that 3-body binding is directly correlated with 2-body binding.*

The relationship of this calculation to data on gaseous He at low temperatures is complicated by shortcomings of both the data and the theory. Virial coefficients are difficult to obtain accurately at low temperatures, since the gas liquifies at quite low pressures; the second virial coefficients could well be in error by 10%, and the third virial coefficients are exceedingly uncertain. This ex-

perimental uncertainty is reflected in a corresponding uncertainty in the 2-body He-He force law; some of the forces fitted in the literature are strong enough to give one discrete bound state for the molecule He_2, others fall just short of doing so.

On the theoretical side, the calculation of the second virial coefficient is on firm ground, but the third virial coefficient is known only in the form of a series, obtained by use of the binary-collisions expansion of Lee and Yang,[11] and in the form of expressions for limiting cases given by Pais and Uhlenbeck.[12] Lee and Yang[11] indicate that the convergence of this expansion is not clearly understood, but have expressed the hope that for interactions for which 3- and more-particle bound states do not exist, the expansion converges. For helium where there are bound states or nearly bound states, we expect the series to converge slowly, if at all, to the correct result. Further, since the numerical evaluation of the series on a computer[1] is limited to the leading few terms, the theory can stand improvement. We are planning to look further into the quantum theory of the third virial coefficient, from the point of view of avoiding the use of slowly convergent expansions.

One main purpose in publishing the present calculation is to bring to the attention of experimentalists the fact that more accurate data on gaseous helium at low temperatures are needed badly, and that such data can probably be interpreted if and when they become available. In particular, second virial coefficients accurate to 1% for temperatures of 1–20°K, and third virial coefficients accurate to 20% in the same temperature range, would make a very significant difference to the analysis.

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[10] A theorem proved by G. Derrick: $\lim_{\sigma \to 0} E(\sigma) = E(0)$, where σ is the diameter of the hard core and E the energy of the n-body bound state. See G. Derrick, Nucl. Phys. 6, 287 (1958).

[11] T. D. Lee and C. N. Yang, Phys. Rev. 113, 1165 (1959).
[12] A. Pais and G. Uhlenbeck, Phys. Rev. 116, 250 (1959).