

significant aspect of the results obtained here are that they may provide a formal link between the Hückel method and the inclusion of antisymmetrization in the LCAO scheme, thus making the analysis of the relationship between the two easier, and, in particular, providing the possibility of transferring whatever physical interpretations may be given to the results of the simple method to those of a more refined calculation. It may also be noticed that our treatment

has been carried out without any limitation to special classes of molecular systems (with the possible exception of those for which Mulliken's approximation does not hold). It therefore may help to make a little clearer the problems involved in the extension of methods primarily conceived and tested for the π -systems of hydrocarbons to electronic systems involving different species of atoms and atomic orbitals.

Intermolecular Forces

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1. INTRODUCTION

THE concept of an intermolecular force between a pair of particles has been of great value in our understanding of a wide range of phenomena and considerable attention has been given in recent years to the problem of deriving the intermolecular forces appropriate to specific atomic and molecular systems. The subject of intermolecular forces was reviewed in 1960 by Buckingham¹ for neutral systems and by Dalgarno² for ionic systems, and this review is concerned mainly with subsequent developments.

2. SEMIEMPIRICAL PROCEDURES

It is appropriate to begin with a description of semiempirical procedures since their application has provided most of our detailed knowledge of intermolecular forces. There are two procedures, one of which employs data on transport coefficients and scattering and the other of which employs spectroscopic data.

2.1 Transport Coefficients

The mathematical theory of nonuniform spherically symmetric gases, developed by Chapman and Enskog,³ reduces the prediction of transport phenomena to the calculation of scattering cross sections

$$Q_l(v) = 2\pi \int_0^\pi I(v, \theta) (1 - \cos^l \theta) \sin \theta d\theta, \quad (1)$$

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¹ R. A. Buckingham, *Planetary Space Sci.* **3**, 205 (1961).

² A. Dalgarno, *Planetary Space Sci.* **3**, 217 (1961).

³ J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954).

where θ is the angle of scattering, v is the relative velocity of the colliding particles, $I(v, \theta)$ is the differential cross section, and l is a positive integer. To a first approximation, the coefficient of diffusion is determined by $Q_1(v)$ and the coefficients of viscosity and thermal conductivity by $Q_2(v)$, while the coefficient of thermal diffusion depends upon $Q_1(v)$ and $Q_2(v)$. Explicit expressions for these various transport coefficients may be derived from formulas given in the treatise of Hirschfelder, Curtiss, and Bird.³

If the interaction potential $V(R)$, R being the separation of the colliding particles, is known, $I(v, \theta)$ can be calculated. Because the factor $(1 - \cos^l \theta)$ in the integrand of (1) suppresses the contribution from small-angle scattering, a classical description of the scattering is usually sufficiently accurate. According to it, the cross sections may be written

$$Q_l(v) = 2\pi \int_0^\infty (1 - \cos^l \theta) p dp, \quad (2)$$

where

$$\theta(p) = \pi - 2p \int_{R_m}^\infty \frac{dR/R^2}{\left[1 - \frac{p^2}{R^2} - \frac{2V(R)}{\mu v^2}\right]^{1/2}}, \quad (3)$$

p being the impact parameter, μ the reduced mass, and R_m the classical distance of closest approach.

For light elements at low temperatures, it may be necessary to use a quantal description of the scattering. According to it

$$Q_1(v) = \frac{4\pi}{k^2} \sum_{s=0}^\infty (s+1) \sin^2(\eta_{s+1} - \eta_s) \quad (4)$$

and

$$Q_2(v) = \frac{4\pi}{k^2} \sum_{s=0}^\infty \frac{(s+1)(s+2)}{(2s+3)} \sin^2(\eta_{s+2} - \eta_s), \quad (5)$$

where k is the wave number $\mu v/\hbar$ and η_s is the phase shift of order s , defined by the requirement that the regular solution of the partial wave equation

$$\frac{d^2\phi_s}{dR^2} + \left[k^2 - \frac{2\mu V}{\hbar^2} - \frac{s(s+1)}{R^2} \right] \phi_s = 0 \quad (6)$$

behave asymptotically as

$$\phi_s(R) \sim k^{-1} \sin(kR - s\pi/2 + \eta_s). \quad (7)$$

The detailed connections between the quantal and classical formulations can be made following the arguments of Ford and Wheeler.⁴ In general if the asymptotic approximation⁵ is employed for the phase shifts and the discrete summations of (4) and (5) are replaced by integrations the quantal formulas become identical to the classical formulas.

The analysis of transport data to yield interaction potentials has been carried out by adopting analytical representations of the potential which contain a number of disposable parameters and choosing the parameters so as to reproduce as closely as possible the available experimental data. Due largely to the work of Hirschfelder and Mason and their collaborators, this procedure has become a powerful and straightforward technique⁶ for systematizing and extending measurements of transport coefficients. The technique has been less useful for determining intermolecular potentials, for the value of the derived potential at any particular separation depends upon the analytical representation that has been used, the potential being correct only in the sense of an average over the intermediate separations which determine the transport coefficients. It follows that care must be exercised in predicting transport coefficients at temperatures outside the measured range.^{1,7}

Additional information about the potentials at small and large separations is required in order to increase the flexibility of the analytical representations and so remove the lack of uniqueness of the derived potentials. Such information can be provided by measurements of scattering.

2.2 Scattering Data

Measurements of the scattering of a beam of par-

⁴ K. W. Ford and J. A. Wheeler, *Ann. Phys. (N. Y.)* **7**, 259 (1959).

⁵ R. A. Buckingham in *Quantum Theory*, edited by D. R. Bates (Academic Press Inc., New York, 1961), Vol. I.

⁶ E. Thornton and W. A. D. Baker, *Proc. Phys. Soc. (London)* **80**, 1171 (1962); A. A. Westenberg and G. Frazier, *J. Chem. Phys.* **36**, 3499 (1962); S. Weissman and E. A. Mason, *J. Chem. Phys.* **36**, 794 (1962); **37**, 1289 (1962). A. A. Westenberg and N. deHaas, *Phys. Fluids* **5**, 266 (1962); B. N. Srivastava and I. B. Srivastava, *J. Chem. Phys.* **36**, 2016 (1962); I. Amdur and L. M. Shuler, *J. Chem. Phys.* **38**, 188 (1962).

⁷ I. Amdur and J. Ross, *Combust. Flame* **2**, 412 (1958).

ticles yield values either of the differential scattering cross section $I(\theta)$ or of the total cross section for scattering through angles greater than some θ_0

$$Q = 2\pi \int_{\theta_0}^{\pi} I(\theta) \sin \theta d\theta, \quad (8)$$

θ_0 depending upon the geometry of the apparatus.

Measurements of scattering constitute a flexible probe into intermolecular forces, since by varying the beam energy and the angle of scattering, it is possible in principle to scan the range from large to small separations. However at high energies the concept of an intermolecular force loses its usefulness and it is not possible to probe directly the potential at very small separations.

2.2.1 High-Energy Measurements

Measurements of the scattering of beams of particles with energies ranging from several eV to a few keV have been carried out by Amdur, Berry, Simmons, Muschlitz, and others and have yielded valuable information on the forces at small separations. Little comment is necessary here since the subject has been reviewed recently by Mason and Vanderslice.⁸ Some more recent studies are referenced in footnote 9.

A comparison of the potential derived from the scattering of He by He with that derived from quantal calculations is discussed in 3.1.1.

2.2.2 Low-Energy Measurements

Measurements of the scattering of beams of neutral particles with thermal energies have been reported at various times during the past thirty years (cf. Massey and Burhop¹⁰) but only recently has a systematic program been pursued. At thermal energies, the scattering is determined mainly by the long-range interaction

$$V(r) \sim -C/r^6. \quad (9)$$

The total cross section corresponding to (9) is given by the Massey-Mohr¹¹ formula as

$$Q = 4.66 \times 10^{11} (C/v)^{2/5} \text{ cm}^2 \quad (10)$$

⁸ E. A. Mason and J. T. Vanderslice in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962).

⁹ G. M. Smith and E. E. Muschlitz, *J. Chem. Phys.* **33**, 1819 (1960); I. Amdur, J. E. Jordan, and S. O. Colgate, *J. Chem. Phys.* **34**, 1525 (1961); W. H. Cramer, *J. Chem. Phys.* **35**, 836 (1961); I. Amdur, M. S. Longmire, and E. A. Mason, *J. Chem. Phys.* **35**, 895 (1961); I. Amdur and R. R. Bertrand, *J. Chem. Phys.* **36**, 1078 (1962); R. D. Cloney and J. T. Vanderslice, *J. Chem. Phys.* **36**, 1866 (1962); C. E. Baker, J. M. McGuire, and E. E. Muschlitz, *J. Chem. Phys.* **37**, 2571 (1962).

¹⁰ H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon Press, Oxford, England, 1952).

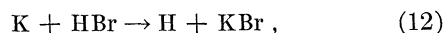
¹¹ H. S. W. Massey and C. B. O. Mohr, *Proc. Roy. Soc. (London)* **A144**, 188 (1934).

and (10) has been widely used. A modification, due to Schiff,¹² suggests that the formula

$$Q = 5.00 \times 10^{11} (C/v)^{2/5} \text{ cm}^2 \quad (11)$$

may be more accurate. Bernstein¹³ has verified by detailed phase-shift calculations that the formulas accurately predict the mean cross sections and he has also analyzed the deviations which occur, showing in particular their relation to the vibrational levels of the molecule formed by the colliding pair.¹⁴ The assumption that (9) is appropriate can be tested by observing¹⁵ the velocity dependence of Q and also by observing¹⁶ the angular dependence of $I(\theta)$. Measurements of $I(\theta)$ can also yield information on the forces at intermediate separations and the rainbow scattering phenomenon⁴ can be related to the depth of the potential well.¹⁷

Of special interest are the crossed-beam experiments initiated by Taylor and Datz.¹⁸ It has proved possible¹⁹ to measure the cross section for chemical reactions such as



yielding detailed information which will be of the greatest value in developing a satisfactory theory of reaction rates.

The scattering of molecular beams has been reviewed recently by Pauly and by Fite and Datz.²⁰ Theory and experiment are in agreement except that the values of the van der Waals coefficients C derived from the analysis of scattering data are apparently uniformly high. A brief comparison is given in 3.3.

2.3 Molecular Gases

The theoretical description that has been used in the analysis of data on transport coefficients and on scattering applies to a spherical gas and assumes that only elastic scattering can occur. A correction for the effect of the internal degrees of freedom on thermal

conductivity has been applied,^{3,21} but otherwise the description has been used without modification for molecular gases, where the intermolecular potential is not spherically symmetric and inelastic-scattering processes occur. The procedure has not revealed any serious inconsistencies and the concept of an intermolecular potential apparently retains its usefulness. This can be understood on the basis of some arguments given by Bernstein, Dalgarno, Percival, and Massey,²² provided it is recognized that the measurements refer not to the elastic-scattering cross sections but to the total cross section. However since the angular distributions resulting from elastic and inelastic scattering are different, real discrepancies will occur between the effective potentials derived from transport data and the effective potentials derived from scattering data, and neither of the effective potentials can be immediately identified with those resulting from quantal calculations.

A principal reason for the success of the analyses is that the spherical and the orientation-dependent parts of the interaction potential between the neutral species involved both fall off as R^{-6} . For the interaction potential between an ion and a molecule, the spherically symmetric part falls off as R^{-4} and the orientation-dependent part as R^{-2} or R^{-3} . The analytic representations adopted for ion-molecule interactions all have the wrong form at large separations and predictions of transport coefficients based upon analyses of scattering data may be seriously misleading.

2.4 Virial Coefficients and Crystal Structure

For the sake of completeness it should be noted that intermolecular potentials can also be derived from virial coefficients^{3,23} and crystal structure.^{3,24}

2.5 Spectroscopic Data

Intermolecular potentials at intermediate separations can be obtained for systems which form stable molecules by application of the Rydberg-Klein-Rees²⁵ procedure to the observed locations of the vibrational levels. Numerous electronic states have been treated by Mason, Vanderslice, and their col-

¹² L. I. Schiff, *Phys. Rev.* **103**, 443 (1956).

¹³ R. B. Bernstein, *J. Chem. Phys.* **33**, 795 (1960); **36**, 1403 (1962).

¹⁴ R. B. Bernstein, *J. Chem. Phys.* **37**, 1880 (1962).

¹⁵ H. Pauly, *Z. Naturforsch.* **15a**, 277 (1960); E. W. Rothe, P. K. Roe, S. M. Trujillo, and R. H. Neynaber, *Phys. Rev.* **128**, 659 (1962).

¹⁶ F. A. Morse and R. B. Bernstein, *J. Chem. Phys.* **37**, 2019 (1962); D. Beck, *J. Chem. Phys.* **37**, 2884 (1962).

¹⁷ F. A. Morse, R. B. Bernstein, and H. V. Hostettler, *J. Chem. Phys.* **36**, 1947 (1962).

¹⁸ E. H. Taylor and S. Datz, *J. Chem. Phys.* **23**, 1711 (1955).

¹⁹ S. Datz, R. Herschbach, and E. H. Taylor, *J. Chem. Phys.* **35**, 1549 (1961); D. R. Herschbach, J. H. Kwei, and J. A. Norris, *J. Chem. Phys.* **34**, 1842 (1961); D. Beck, *J. Chem. Phys.* **37**, 2884 (1962); D. Beck, E. F. Greene, and J. Ross, *J. Chem. Phys.* **37**, 2895 (1962).

²⁰ H. Pauly, *Fortschr. Physik* **9**, 613 (1961); W. L. Fite and S. Datz, *Ann. Rev. Phys. Chem.* (to be published).

²¹ E. A. Mason and L. Monchick, *J. Chem. Phys.* **36**, 1622, 2746 (1962).

²² R. B. Bernstein, A. Dalgarno, H. S. W. Massey, and I. C. Percival, *Proc. Roy. Soc. (London)* (to be published).

²³ Cf. D. D. Konowalow and J. O. Hirschfelder, *Phys. Fluids* **4**, 629 (1961) and **5**, 126 (1962); H. W. Schamp, E. A. Mason, and K. Su, *Phys. Fluids* **4**, 769 (1961).

²⁴ Cf. E. A. Guggenheim and M. L. McGlashan, *Proc. Roy. Soc. (London)* **A255**, 456 (1960).

²⁵ R. Rydberg, *Z. Physik* **73**, 376 (1931); **80**, 514 (1933); O. Klein, *Z. Physik* **76**, 226 (1932); A. L. G. Rees, *Proc. Phys. Soc. (London)* **A59**, 998 (1947).

laborators.²⁶ An approximate scheme based upon the assumption of perfect pairing has been used to obtain potentials for repulsive states²⁷ which may be correct to within a factor of two.²⁸ This work has led to more precise predictions of the transport properties of high-temperature air.²⁹

Some care is needed in using intermolecular potentials derived from spectroscopic data since the potential curve along which the atoms separate adiabatically may not be that along which they approach adiabatically.

It is appropriate here to draw attention to the work on analytical representations of the intermolecular potentials for bound molecular states, which are valuable when application of the Rydberg–Klein–Rees procedure is not possible. Some references are given in footnote 30.

3. QUANTAL CALCULATIONS

It is convenient to distinguish between short-range, intermediate-range, and long-range calculations.

3.1 Short-Range Calculations

At very small separations, perturbation and variational methods can be developed based upon a united-atom description which yield directly the energies of interaction and some preliminary work in this direction has been reported.³¹ The convergence becomes slow as the separation increases and the only general procedure that has been successfully used at small separations is the Hartree–Fock approximation. The procedure suffers from the obvious defect that the evaluation of a small quantity is achieved by subtracting one large quantity from another and it is not

²⁶ J. T. Vanderslice, E. A. Mason, W. G. Maisch, and E. R. Lippincott, *J. Chem. Phys.* **33**, 614 (1960); R. J. Fallon, J. T. Vanderslice, and E. A. Mason, *J. Chem. Phys.* **33**, 944 (1960); R. J. Fallon, I. Tobias, and J. T. Vanderslice, *J. Chem. Phys.* **33**, 1638 (1960); I. Tobias and J. T. Vanderslice, *J. Chem. Phys.* **35**, 1852 (1961); J. T. Vanderslice, *J. Chem. Phys.* **37**, 384 (1962); S. M. Read and J. T. Vanderslice, *J. Chem. Phys.* **36**, 2366 (1962); S. M. Read, J. T. Vanderslice, and F. Jenc, *J. Chem. Phys.* **37**, 205 (1962).

²⁷ J. T. Vanderslice, E. A. Mason, W. G. Maisch, and E. R. Lippincott, *J. Chem. Phys.* **33**, 614 (1960).

²⁸ J. T. Vanderslice and E. A. Mason, *J. Chem. Phys.* **33**, 492 (1960).

²⁹ A. Dalgarno and F. J. Smith, *Planetary Space. Sci.* **9**, 1 (1962); K. S. Yun and E. A. Mason, *Phys. Fluids* **5**, 380 (1962); K. S. Yun, S. Weissman, and E. A. Mason, *Phys. Fluids* **5**, 672 (1962).

³⁰ D. Steele and E. R. Lippincott, *J. Chem. Phys.* **35**, 2065 (1961); E. R. Lippincott, D. Steele, and P. Caldwell, *J. Chem. Phys.* **35**, 123 (1961); W. L. Clinton, *J. Chem. Phys.* **36**, 555, 556 (1962); H. W. Woolley, *J. Chem. Phys.* **37**, 1307 (1962).

³¹ W. A. Bingel, *Z. Naturforsch.* **12a**, 59 (1957); *J. Chem. Phys.* **30**, 1250, 1254 (1959); *J. Chem. Phys.* **38**, 274 (1963); R. A. Buckingham, *Trans Faraday Soc.* **54**, 453 (1958); R. A. Buckingham and D. M. Dupare in *Progress in International Research on Thermodynamics and Transport Properties*, Second Symposium (Academic Press Inc., New York, 1962); *J. Chem. Phys.* **38**, 275 (1963).

yet established that the interaction energies will be larger than the unavoidable errors. Much will depend upon the behavior of the correlation energy as a function of nuclear separation.

Because of the remarkable efficiency of the programs devised under the guidance of Roothaan and Nesbet it is practicable for simple systems to carry out more accurate calculations which include configuration mixing. These calculations are of great importance as is demonstrated by the example of the interaction between two helium atoms.

3.1.1 The He–He Interaction

The interaction between two helium atoms has been the subject of many studies. A list of references is given by Phillipson³² to which should be added a paper by Kim.³³ The most accurate calculations at short distances are those of Phillipson who uses a multi-configuration molecular wave function. His values are higher than those derived from the conventional analysis of Amdur's data,³⁴ the discrepancy increasing with decreasing separation and attaining a value of about 9 eV at a separation of 0–5 Å. Using the argument that the correlation energy is roughly constant over the entire range of separations, Phillipson claims that his error is less than 0.6 eV. Although this may be an underestimate, the origin of correlation in Be and in He being so different, the accuracy is undoubtedly sufficient to suggest that a fundamental error exists in the analysis of the scattering data. It appears from recent work of Thorson³⁵ that at the velocities necessary to penetrate the region of small separations the collisions are not adiabatic and the concept of an intermolecular potential is not appropriate.

3.2 Intermediate Separations

The calculation of the forces at intermediate separations is a difficult problem. The Hartree–Fock approximation does not, except in a few special cases, dissociate into the correct limits and the interaction energy is only a small fraction of the correlation energy. Yet precise calculations are necessary. Thus, the potential-energy curve corresponding to the stable molecule formed by the approach of a normal and a metastable helium atom has a repulsive barrier

³² P. E. Phillipson, *Phys. Rev.* **125**, 1981 (1962).

³³ D. Y. Kim, *Z. Physik* **166**, 359 (1962).

³⁴ I. Amdur, *J. Chem. Phys.* **17**, 844 (1949); I. Amdur and A. L. Harkness, *J. Chem. Phys.* **22**, 664 (1954); I. Amdur, J. E. Jordan, and S. O. Colgate, *J. Chem. Phys.* **34**, 1525 (1961); J. Amdur and R. R. Bertrand, *J. Chem. Phys.* **36**, 1078 (1962).

³⁵ W. Thorson (private communication).

at intermediate separations.³⁶ Such barriers can markedly affect the behavior of a chemical reaction.

It is essential that the wave function employed at intermediate separations should accurately reproduce the forces at large separations. This is most easily achieved by first solving the long range interaction problem and then incorporating the solution in the wave function at intermediate separations. Calculations of this kind have been reported by Hirschfelder and Linnett³⁷ for H₂ and by Moore³⁸ and Kim³³ for He₂.

3.3 Large Separations

At large separations, the molecular wave function can be written

$$\Psi = \psi_0 + \psi_1, \quad (13)$$

where, in the absence of degeneracies, ψ_0 is the product of the wave functions of the approaching atoms a and b

$$\psi_0 = \phi_a(\mathbf{r}_a)\chi_b(\mathbf{r}_b) \quad (14)$$

and ψ_1 is the correction which takes account of the mutual perturbation. If H_a and H_b are, respectively, the Hamiltonians of the two atoms and E_a^0 and E_b^0 are their eigenvalues, then to first order in the instantaneous interaction $v_{ab}(\mathbf{r}_a, \mathbf{r}_b, R)$, ψ_1 is the solution of the equation

$$(H_a + H_b - E_a^0 - E_b^0)\psi_1 + [v_{ab} - \langle \psi_0 | v_{ab} | \psi_0 \rangle] \psi_0 = 0. \quad (15)$$

To third order in v_{ab} , the interaction potential is

$$V(R) = \langle \psi_0 | v_{ab} | \psi_0 \rangle + \langle \psi_1 | v_{ab} | \psi_0 \rangle + \langle \psi_1 | v_{ab} | \psi_1 \rangle, \quad (16)$$

provided (15) is solved subject to the requirement that

$$\langle \psi_1, \psi_0 \rangle = 0. \quad (17)$$

Equation (15) may be solved by minimizing the functional

$$\langle \psi_1 | H_a + H_b - E_a^0 - E_b^0 | \psi_1 \rangle + 2\langle \psi_1 | v_{ab} - \langle \psi_0 | v_{ab} | \psi_0 \rangle | \psi_0 \rangle \quad (18)$$

for some trial form of ψ_1 . High accuracy is to be anticipated from trial functions containing only a few parameters but in no case has a solution yet been attempted.

Except for the simplest atomic systems, the cal-

culations encounter the difficulty (as do all calculations of intermolecular forces) that the wave functions of the separated atoms are known only approximately. This difficulty can be treated in a systematic manner if the Hartree-Fock approximation is used to describe the atoms.³⁹

At very large separations, v_{ab} can be expanded in inverse powers of the separation⁴⁰ and considerable simplification results provided it suffices to retain only one or two terms. For neutral atoms in non-degenerate states, the leading term of $V(R)$ is given by

$$V(R) = -C/R^6. \quad (19)$$

Calculations of C based upon (18) have been carried out by Slater and Kirkwood⁴¹ and, using superficially different procedures, by Buckingham⁴² and by Knipp.⁴³ The relationship between their results and the connection with various approximate formulas can be found using arguments similar to those presented in an analysis of methods of calculating atomic polarizabilities.⁴⁴

A major difficulty confronting attempts to improve calculations of C was the lack of reliable comparison data, as evidenced by the reviews of Margenau⁴⁵ and of Pitzer.⁴⁶ This difficulty has been met by using the formula for C that results from formally solving (15) by expanding ψ_1 in terms of the complete set of eigenfunctions of the two atoms at an infinite distance apart.⁴⁷

The values of C for Ar-He, Ar-Ne, and Ar-Ar⁴⁸ may be directly compared with values derived from scattering measurements⁴⁹:

	Ar-He	Ar-Ne	Ar-Ar
Predicted	10	21	68
Measured	25	60	180

Since the error in the theoretical predictions is unlikely to exceed 10%, a large discrepancy emerges and

³⁹ A. Dalgarno (to be published, 1963).

⁴⁰ A general formulation has been given by P. R. Fontana, Phys. Rev. **123**, 1865 (1961); **123**, 1871 (1961); **125**, 1597 (1962).

⁴¹ J. C. Slater and J. G. Kirkwood, Phys. Rev. **37**, 682 (1932).

⁴² R. A. Buckingham, Proc. Roy. Soc. (London) **A160**, 112 (1937).

⁴³ J. K. Knipp, Phys. Rev. **55**, 1244 (1939).

⁴⁴ A. Dalgarno, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1962), Vol. 11, p. 281.

⁴⁵ H. Margenau, Rev. Mod. Phys. **11**, 1 (1939).

⁴⁶ K. S. Pitzer, Advan. Chem. Phys. **2**, 59 (1959).

⁴⁷ Cf. A. Dalgarno, Rev. Mod. Phys. **35**, 611 (1963).

⁴⁸ A. Dalgarno and A. E. Kingston, Proc. Phys. Soc. (London) **78**, 607 (1961).

⁴⁹ E. W. Rothe, L. L. Marino, R. H. Neynaber, P. K. Roe, and T. P. Das, Phys. Rev. **126**, 594 (1962).

³⁶ R. A. Buckingham and A. Dalgarno, Proc. Roy. Soc. (London) **A213**, 327 (1952).

³⁷ J. O. Hirschfelder and J. W. Linnett, J. Chem. Phys. **18**, 130 (1950).

³⁸ N. Moore, J. Chem. Phys. **33**, 471 (1960).

the methods of analyzing the experimental data should be subjected to careful scrutiny.

3.3.1 Divergence of Series Representations

The series representation of $V(R)$ obtained by expanding v_{ab} in powers of R^{-1} diverges and there has been some discussion as to how the divergence may be removed. However, according to Dalgarno and Lewis⁵⁰ the series so obtained is unique so that if one wishes to use an expansion in R^{-1} , the divergence cannot be avoided. The series is actually asymptotically divergent and can be evaluated by truncating it at any particular term. If the inaccuracy so introduced, which is of the order of the last term retained, is too large then it seems best not to expand v_{ab} . It may be noted that if more than the first two or three terms are required, it is actually less laborious to retain the exact form of v_{ab} . The detailed connection between $V(R)$ and its expansion is shown in a study by Dalgarno and Lynn⁵¹ in which a particular case is solved exactly.

4. THE BORN-OPPENHEIMER APPROXIMATION

The concept of an intermolecular force requires that an effective separation of the nuclear and electronic motion can be made. This separation is achieved in the Born–Oppenheimer approximation³ and several investigations of its accuracy have been made.⁵² For simple systems in states of zero angular momentum, the discussion is straightforward and it

appears that the errors involved in the use of an intermolecular force are too small to be detected experimentally. For atoms in states of nonzero angular momentum and especially for atoms in excited states, more care is necessary. The notion of an intermolecular force can still be preserved (for a more limited range of physical conditions) provided it is recognized that the coupling scheme for the nuclear and electronic angular momentum is a function of nuclear separation.⁴⁰

Closely related to the validity of the Born–Oppenheimer approximation is the notion of adiabaticity. In the interpretation of scattering data and of transport phenomena, it is necessary to take account of the possibility, even at low velocities, that some of the collisions may be nonadiabatic. Thus, in the collisions of an oxygen atom in the 3P_2 state with another system, a certain fraction will leave the oxygen atom in the 3P_1 state.

There is little doubt that the concept of an intermolecular force is too great an oversimplification to account for all the detailed effects associated with the collision broadening of spectral lines in neutral gases but it may suffice to explain the observed shifts.⁵³ It is interesting to note that the differences in the forces between an atom in one hyperfine level and a perturbing molecule and an atom in a second hyperfine level and a perturbing molecule are of great importance.⁵⁴ These differences are also significant in the interpretation of the spectra of atoms trapped in a solid matrix.⁵⁵ The development of methods for the precise calculation of these differences would be of considerable value.

⁵⁰ A. Dalgarno and J. T. Lewis, Proc. Phys. Soc. (London) **A69**, 57 (1956).

⁵¹ A. Dalgarno and N. Lynn, Proc. Phys. Soc. (London) **A70**, 233 (1957).

⁵² T. Y. Wu and A. B. Bhatia, J. Chem. Phys. **24**, 48 (1956); A. Dalgarno and R. W. McCarroll, Proc. Roy. Soc. (London) **A237**, 383 (1956); **A239**, 413 (1957); D. W. Jepsen and J. O. Hirschfelder, J. Chem. Phys. **32**, 1323 (1960); W. Kobos and L. Woliniewicz, Acta Phys. Polon. **20**, 129 (1961); A. Froman, J. Chem. Phys. **36**, 1490 (1962).

⁵³ M. Arditì and T. R. Carver, Phys. Rev. **112**, 449 (1958); P. L. Bender and A. R. Chi, Phys. Rev. **112**, 450 (1958).

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Discussion on Intermolecular Forces

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PITZER: First, may I say how much we welcome Dalgarno's calculations of the coefficients of the R^{-6} term which are a real improvement over earlier work. The disagreement with scattering data, to which he has referred, is similar to the discrepancy I pointed out many years ago between the coefficient of the R^{-6} term from viscosity or second virial coefficient data and the values from the London formula using polarizability and ionization potential values. The values agreed fairly well for H_2 and He but, for heavier rare gases and some other molecules, the values from the London formula are only about half those required to fit the viscosity or volumetric data. Donath developed a probable explanation of this factor, and I believe Sinanoğlu also has ideas on this point.

It is possible to get reasonably good potential curves to dissociation from LCAO–MO wave