

should be such that second-order exchange interactions are relatively unimportant at small interatomic separations, otherwise the validity of a Heitler-London type of calculation for the binding energy of the hydrogen molecule remains unexplained. We note that, on the basis of the definitions H_0 and H' [Eq. (5)], the Heitler-London analysis corresponds precisely to a first-order perturbation treatment for the energy of interaction between two hydrogen atoms.

In certain problems the fact that the Unsöld average energies are not known plays only a minor role. In particular, this is the case when we are essentially interested in *relative* perturbation energies, e.g., in simultaneous interactions between three atoms *relative* to the sum of pair interactions between the atoms, as occurs in the problem of crystal stability for molecular and ionic solids.^{15,16} We have carried out a quantitative comparison between results obtained by different perturbation methods, as applied to this problem of

many-atom interactions and crystal stability. These results will be reported separately.

The analysis presented here adds nothing to a solution of the difficult problem concerning convergence properties of perturbation series; for more details we refer to the review article by Herring.¹⁴ The principal assumption inherent in these perturbation procedures is that terms of higher order constitute at most a modification of the van der Waals interactions between the atoms or molecules.

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Transition Matrix Elements for Large Momentum or Energy Transfer*

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The radial matrix element $M = \int_0^\infty R_{kl'}(r) j_L(qr) R_{nl}(r) r^2 dr$, which appears in collision theory and photon absorption ($L=1$, $q \sim 0$), has been studied in the past for hydrogenic wave functions. Its behavior for large q or large k is now shown to depend only on the expansion of the wave functions near the nucleus and on an application of selection rules. For large q , the trend is $M \propto q^{-(l+l'+4)}$ and for large k and normalization per unit energy, $M \propto k^{-(l+L+1/2)} q^L$. The asymptotic trend of Altshuler's equivalent forms of the matrix elements is discussed.

THE Born approximation to the theory of inelastic collisions of charged particles with atoms involves the generalized form factor $\int \Psi_j^* \sum_i \exp(i\mathbf{q} \cdot \mathbf{r}_i) \Psi_i d\tau$, where $\hbar\mathbf{q}$ is the momentum transfer, \mathbf{r}_i is the position of the i th electron, Ψ_i and Ψ_j are the initial and final wave functions of the atom, respectively, and $\int d\tau$ covers all coordinates. The dipole integral which determines photon absorption is the low- q limit of this matrix element. Expansion of $\exp(i\mathbf{q} \cdot \mathbf{r}_i)$ into spherical waves and assumption of a determinant form for the many-electron wave functions reduce the non-trivial portion of the form factor to the single-electron radial integral

$$M = \int_0^\infty R_{kl'}(r) j_L(qr) R_{nl}(r) r^2 dr, \quad (1)$$

where the spherical Bessel function is defined

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as

$$j_L(qr) = [\pi/2qr]^{1/2} J_{L+1/2}(qr), \quad (2)$$

and where the final state kl' of the electron may belong to the discrete or to the continuous spectrum, whereas nl is bound. [The simplifying assumption of determinant wave functions is actually unnecessary. One could replace the product $R_{kl'} R_{nl}$ by a coefficient of the spherical wave expansion of the one-particle reduced density matrix $\int \Psi_j^* \Psi_i \prod_{j>1} d\mathbf{r}_j$ and proceed along the same lines as in this paper.] In the expansion of the form factor, the radial integral M is multiplied by an angular integral of the form

$$\int Y_{l'm'}^*(\theta, \varphi) P_L(\cos\theta) Y_{lm}(\theta, \varphi) d\Omega.$$

The parity selection rule and the triangular condition that are implied in this integral will be of importance in determining the asymptotic behavior of M .

The integral (1) and especially its particular case $L=1$, $q \sim 0$ have been calculated analytically for

hydrogenic wave functions R_{nl} .^{1,2} This paper investigates the behavior of M for large values of q or of the final-state wave number k under broader circumstances. This behavior has been often implied in literature, but apparently was never stated or derived.

For large values of q (or k) one of the factors in the integrand of (1) oscillates very rapidly. Therefore, the main contribution to (1) arises from small values of r , of order q^{-1} (or k^{-1}). The integral can then be evaluated by expanding the slowly varying factors of the integrand into powers of r , which yields an expansion of (1) into powers of q^{-1} (or k^{-1}). The coefficients of this expansion are determined by nontrivial normalization conditions and by solving the Schrödinger equation for the radial functions R by expansion into powers of r . This solution is simple because the atomic potential is Coulombic, or near-Coulombic, near the nucleus;

$$V(r) = A/r + B + Cr + \dots \quad (3)$$

[Any term $\propto r^{-2}$ in this expansion could be combined with the centrifugal term, introducing an effective quantum number \bar{l} in the radial equation.] The calculation of (1) by expanding the radial functions into powers of r is equivalent to Lassette's³ procedure of successive integration by parts of the integral (1) for S states of the He atom and is discussed in the Appendix.

For application to large q , we set

$$R_{nl} = b_0 r^l + b_1 r^{l+1} + \dots, \quad (4)$$

$$R_{k\nu} = f_0 r^\nu + f_1 r^{\nu+1} + \dots \quad (5)$$

The coefficients b_0 and f_0 are determined by normalization conditions whose application requires, in principle, a complete integration of the radial equations. However, they are related directly or by dispersion relations⁴ to parameters like hyperfine separations, isotope shifts, and scattering phase shifts, from which they might be estimated. The ratios of the successive coefficients b_1/b_0 , b_2/b_0 , \dots , f_1/f_0 , \dots depend instead on integration near the nucleus, i.e., on the energies E_{nl} and $E_{k\nu}$ and on the coefficients A , B , C , \dots . Substitution of (4) and (5) into (1) and the application of a standard formula⁵ yields

$$\begin{aligned} M &= \sum_s C_s \int_0^\infty r^{l+\nu+2+s} j_L(qr) dr \\ &= \sum_s C_s (\sqrt{\pi}) 2^{l+\nu+1+s} q^{-(l+\nu+3+s)} \\ &\quad \times \Gamma[\tfrac{1}{2}(l+\nu+L+3+s)] / \Gamma[\tfrac{1}{2}(L-l-\nu-s)], \quad (6) \end{aligned}$$

¹ N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Clarendon Press, Oxford, England, 1965), 3rd ed., Chap. 16, Sec. 8.

² H. A. Bethe, in *Handbuch der Physik*, edited by H. Geiger and K. Scheel (Julius Springer, Berlin, 1933), Vol. 24/1, Secs. 47 and 52.

³ E. N. Lassette, *J. Chem. Phys.* **43**, 4479 (1965).

⁴ M. L. Goldberger and K. M. Watson, *Collision Theory* (John Wiley & Sons, Inc., New York, 1964), Chap. 6.

⁵ G. N. Watson, *A Treatise on the Theory of Bessel Functions* (Cambridge University Press, Cambridge, England, 1944), 2nd ed.

where

$$C_0 = b_0 f_0, C_1 = (b_1 f_0 + b_0 f_1), \dots \quad (7)$$

The convergence of the expansion of M in (6) is ensured by the exponential behavior of the bound-state wave function R_{nl} for large r . The convergence of the infinite integrals in (6) is discussed in the Appendix.

An essential feature of the expansion (6) is that all terms with even s vanish in any practical application. The argument of the Γ function in their denominators is a nonpositive integer because the angular integral, which always multiplies (1), vanishes unless $L-l-\nu'$ is even (parity-selection rule) and unless $L-l-\nu' \leq 0$ (triangular condition). By the same token, each term with odd s is nonzero. Therefore, the asymptotic behavior of M is determined by the $s=1$ term of (6);

$$M = O[q^{-(l+\nu'+4)}], \quad \text{for } q \rightarrow \infty. \quad (8)$$

This result is known for the special case $l=0$, $\nu'=L$ from the study of the H atom.²

In practice, final states with different ν' are available for each value of k in the continuum. Transitions to the states with lowest ν' , namely, $\nu' = |L-l|$ will predominate for large q . In the presence of configuration interaction, contributions to M from pairs $R_{k\nu'} R_{nl}$ with different values of $l+\nu'$ are superposed. It may then happen that the contribution with the lowest value of $l+\nu'$ predominates for large q only, whereas other contributions are more important for moderate q .

An apparent contradiction with this result emerges by comparison with Altshuler's⁶ alternative expressions of the generalized form-factor integral, which are derived from one another by means of the Schrödinger equations for Ψ_i and Ψ_j . These forms are analogous to the dipole, dipole velocity, and dipole-acceleration matrix elements utilized in the theory of radiative transitions. It was kindly pointed out to us by Dr. R. L. Platzman and Dr. M. Inokuti that Altshuler's "velocity" formula (5) appears to behave asymptotically as $q^{-(l+\nu'+2)}$, in contrast with (8) of this paper. We attribute this discrepancy to the following circumstance: Derivation of the correct high- q behavior requires, of course, the use of *sufficiently* accurate wave functions. The derivation of (8) hinges on the selection rules for the integrals over the angular dependence of the single-electron wave functions, which dependence is exact in any central-field approximation. Thereby, the $s=0$ term of (6) vanishes exactly and any error in the radial solutions $R(r)$ can affect only the *value* of the coefficient (C_1) of the following nonzero term $s=1$. The Altshuler transformation intermixes the radial and angular dependences of the wave functions through the introduction of the operator $\mathbf{q} \cdot \text{grad}$. The quantity corresponding to our radial M is then $iq/2\Delta E$ times the integral that appears in Eq. (3) of the Altshuler paper. In the asymptotic behavior, the leading term of this integral has the dependence $q^{-(l+\nu'+3)}$ and consequently

⁶ S. Altshuler, *Phys. Rev.* **87**, 992 (1952); **89**, 1093 (1953).

the leading term in the matrix element behaves like $q^{-(l+l'+2)}$. Examination of the leading term shows it to have a coefficient that involves C_1 and which actually vanishes, but *only if* C_1/C_0 has the correct value, provided that sufficiently accurate wave functions are used.

Finally, consider the case where k is large and larger than q . The Schrödinger equation that governs $R_{kl}(r)$ reduces to the Bessel equation for $j_{l'}(kr)$ provided that

$$k \gg 2mA/\hbar^2, \quad k^2 \gg 2mB/\hbar^2, \quad \dots, \quad (9)$$

where A, B, \dots are the coefficients of (3). Therefore, we can enter in (1)

$$R_{kl}(r) \sim N_k j_{l'}(kr) \quad (10)$$

to lowest order in k^{-1} . If R is to be normalized per unit energy range, we set⁷

$$N_k = [2mk/\pi\hbar^2]^{1/2}. \quad (11)$$

The product $R_{nl}(r)j_L(qr)$ in the integrand of (1) can now be expanded into powers of r , the lowest term being

$$R_{nl}(r)j_L(qr) = [b_0 q^L / (2L+1)!!] r^{l+L} + \dots \quad (12)$$

Once again, as in (6), the leading term of the expansion of (1) would be of order $k^{-(l+L+5/2)}$, taking (11) into account, but its coefficient vanishes. Therefore, we have

$$M = O[k^{-(l+L+7/2)}], \quad (13)$$

but the coefficient of the first nonvanishing term will already depend on corrective terms to (10). The special case of the dipole transition ($L=1$), namely, $M = O(k^{-l-9/2})$, is well known in the hydrogenic approximation.² It has also been derived⁸ for photoabsorption in helium utilizing the circumstance that a Born approximation equivalent to (10) can be applied to the ejected electron in the high-energy limit.

⁷ L. D. Landau and E. M. Lifschitz, *Quantum Mechanics: Nonrelativistic Theory* (Pergamon Press, Ltd., London, 1958), Chap. 5, Sec. 33.

⁸ P. K. Kabir and E. E. Salpeter, *Phys. Rev.* **108**, 1256 (1957).

APPENDIX

The integral in (6) is of the type

$$\int_0^\infty r^b J_a(qr) dr = 2^b q^{-b-1} \Gamma[\frac{1}{2}(a+b+1)] / \Gamma[\frac{1}{2}(a-b+1)],$$

which is given in Eq. (1), Sec. 13.24 of Ref. 5 under the conditions $\text{Re}(a+b) > -1$ and $\text{Re}(b) < \frac{1}{2}$. These conditions are not fulfilled in our application. However, the convergence of (1) rests on the exponential decay of $R_{nl}(r)$. Therefore it is appropriate to factor out of this decay a factor $\exp(-\epsilon r)$, where ϵ is a small positive number, before carrying out the expansion (4). The integrals are then of the type

$$\int_0^\infty e^{-\epsilon r} r^{l+l'+2+s} j_L(qr) dr,$$

whose value is proportional to $F(\frac{1}{2}[l+l'+L+3+s], \frac{1}{2}[L-l-l'-1-s], L+\frac{3}{2}, q^2/[q^2+\epsilon^2])$ according to Eq. (3), Sec. 13.2 of Ref. 5, for $\epsilon > 0$. In the limit $\epsilon \rightarrow 0$, this hypergeometric function reduces to a product of Γ functions and thereby leads to the result on the right-hand side of (6).

Alternatively, one can integrate (1) by parts³ in succession, utilizing the factor $\exp(\pm iqr)$ of the representation

$$J_L(qr) = \exp(iqr) \sum_{s=0}^L a_s(qr)^{-s-1} + \text{c.c.}$$

[Ref. 5, Eq. (1) of Sec. 3.4]. This procedure yields directly a series in powers of q^{-1} . The integrated terms vanish at $r = \infty$ because of the factor R_{nl} , but vanish at $r=0$ only if they contain a positive power of r . Thereby the integration introduces the successive derivatives of the product $R_{kl}(r)R_{nl}(r)$ at $r=0$ (that is, the coefficients C_s) directly into the final result without any advance reference to the expansions (4) and (5).