and the corrected transverse dispersion relation will be

$$\omega^2=(\omega_0+\omega_1)^2\cong\omega_0^2+2\omega_0\omega_1=\omega_0^2-3\omega_p^4q^2/40\omega_0^2K_F^2, \quad (28)$$

with ω_0^2 given by the first three terms of Eq. (15). Since for physical reasons we must restrict our treatment to $q\ll K_F$ as discussed before and the exchange correction is then small compared to the zero-order frequency, the approach of calculating spin and exchange contributions separately is justified.

IV. CONCLUSION

Taking the ratio of spin to exchange corrections from Eqs. (15) and (28) gives

$$\frac{10}{3}\frac{\hbar^2q^2K_F^2}{m^2\omega_p^2}\ll\frac{10}{3}\frac{\hbar^2K_F^4}{m^2\omega_p^2}\cong10^{-2} \quad (29)$$

for a typical metal, indicating that for the region $q\ll K_F$, particle exchange is more significant than the spin interaction. This is hardly surprising since the typical metal at zero temperature is certainly nonrelativistic whereas particle statistics are important in this system. An interesting feature of the calculation is that when spin and exchange effects are included, the transverse and longitudinal modes are still decoupled in the sense of having separate dispersion relations, at least for first order. They are not entirely independent, however, since the exchange contribution to the transverse relation arises directly from the Coulomb interaction. Thus, even in the "zero interaction" limit to which the self-consistent field treatment corresponds, the indistinguishability of the particles gives rise to currents which couple the radiating and nonradiating modes.

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Quantum-Mechanical Sum-Rule for Infinite Sums Involving the Operator $\partial H/\partial\lambda$*†

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The sum-rule

$$\sum_n{}'\frac{\langle m|A|n\rangle\langle n|\partial\Omega/\partial\lambda|m\rangle+\langle m|\partial\Omega/\partial\lambda|n\rangle\langle n|A|m\rangle}{\epsilon_n-\epsilon_m}=\left\langle m\left|\frac{\partial A}{\partial\lambda}\right|m\right\rangle-\frac{\partial}{\partial\lambda}(\langle m|A|m\rangle)$$

is derived. In this relation $|m\rangle$, $\cdots$, $|n\rangle$, $\cdots$ form a complete set of orthonormal vectors, which are the eigenvectors of the Hermitian linear operator Ω, with eigenvalues ϵ_m, $\cdots\epsilon_n$, $\cdots$; λ is a parameter which occurs in Ω, and A is an arbitrary linear operator. In many sums of this type, Ω is the Hamiltonian operator H. Particular examples are considered, and a differential equation, relating the mass dependence and coordinate dependence of the wave function ψ, is derived.

1. INTRODUCTION

INFINITE sums of the form

$$S\equiv\sum_n{}'\frac{\langle m|A|n\rangle\langle n|B|m\rangle}{\epsilon_n-\epsilon_m} \quad (1)$$

appear in many quantum-mechanical problems. In (1), A and B are linear operators, while $|m\rangle$, $\cdots|n\rangle$, $\cdots$ form a complete set of orthonormal vectors, which are the eigenvectors of some Hermitian linear operator Ω, with eigenvalues ϵ_m, $\cdots\epsilon_n$, $\cdots$; the prime in the summation sign indicates that the summation is over all states except $|n\rangle\equiv|m\rangle$. A familiar case occurs when Ω is identical with the Hamiltonian operator H, so that the ϵ_n's become the energies E_n associated with the different stationary states $|n\rangle$. The summation in S then includes, of course, an integral over the continuum states.

The reduction of S to a simple expression which depends on the properties of $|m\rangle$ alone has long been a challenging problem. A very simple, though dangerously uncertain, expression can be obtained by using the closure approximation.[1] Clinton[2] seems to have been the first to discover a case where, although one of the two operators A and B remains completely arbitrary, S is exactly reducible. He treated those sums in which one operator is identical to $2T-\sum_i\mathbf{r}_i\cdot(\partial V/\partial\mathbf{r}_i)$ (T=kinetic energy operator, V=potential energy operator), while the other operator remains arbitrary,

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[1] A. Unsöld, Z. Physik **43**, 563 (1927).

[2] W. L. Clinton, private communication to the author (to be published).

and he showed that

$$\sum_n{}' \frac{\langle m|2T-\sum_i \mathbf{r}_i\cdot(\partial V/\partial \mathbf{r}_i)|n\rangle\langle n|A|m\rangle}{E_n-E_m} = -\langle m|\sum_i \mathbf{r}_i\cdot\nabla_i(A|m)\rangle-\tfrac{3}{2}N\langle m|A|m\rangle, \quad (2)$$

where the summation indicated by $\sum_i$ is over all particles i, with coordinates $\mathbf{r}_i$, of the system; N represents the total number of particles, and E_n is the energy eigenvalue corresponding to $|n\rangle$.

In the present paper we consider the set of sums

$$S_0\equiv\sum_n{}' \frac{\langle m|A|n\rangle\langle n|\partial\Omega/\partial\lambda|m\rangle}{\epsilon_n-\epsilon_m}, \qquad S_0'\equiv\sum_n{}' \frac{\langle m|\partial\Omega/\partial\lambda|n\rangle\langle n|A|m\rangle}{\epsilon_n-\epsilon_m}, \quad (3)$$

where λ is some parameter which appears in Ω. If A is a Hermitian operator, $S_0'\equiv S_0^*$, where S_0^* is the complex conjugate of S_0. If A is anti-Hermitian, $S_0'\equiv -S_0^*$. These sums have an extremely simple value in terms of matrix elements involving $|m\rangle$ alone. The general formula is, as proven below,

$$S_0+S_0' \equiv\sum_n{}' \frac{\langle m|A|n\rangle\langle n|\partial\Omega/\partial\lambda|m\rangle+\langle m|\partial\Omega/\partial\lambda|n\rangle\langle n|A|m\rangle}{\epsilon_n-\epsilon_m} = \left\langle m\left|\frac{\partial A}{\partial\lambda}\right|m\right\rangle-\frac{\partial}{\partial\lambda}(\langle m|A|m\rangle). \quad (4)$$

This sum-rule is contained implicitly in previous calculations by Epstein, Brown,[3] and possibly others, but it has never, to the author's knowledge, been given as such or used before in simple applications.

2. PROOF

Let us consider the matrix element $\langle n|\partial\Omega/\partial\lambda|m\rangle$. We rewrite it as

$$\left\langle n\left|\frac{\partial\Omega}{\partial\lambda}\right|m\right\rangle=\frac{\partial}{\partial\lambda}(\langle n|\Omega|m\rangle) -\left(\left\langle\frac{\partial n}{\partial\lambda}\right|\Omega\left|m\right\rangle+\left\langle n\right|\Omega\left|\frac{\partial m}{\partial\lambda}\right\rangle\right), \quad (5)$$

where $|\partial n/\partial\lambda\rangle$ is an abbreviated notation for the state represented, in the coordinate representation, by the wave function $\partial\psi_n/\partial\lambda$, ψ_n being the wave function representing the state $|n\rangle$. The first term on the right-hand side of (5) is zero, since $|m\rangle$ is an eigenvector of Ω and since all the eigenvectors form a complete orthogonal set ($\langle m|n\rangle=0$ for $m\neq n$). Hence

$$\left\langle n\left|\frac{\partial\Omega}{\partial\lambda}\right|m\right\rangle=-\epsilon_m\left\langle\frac{\partial n}{\partial\lambda}\right|m\right\rangle-\epsilon_n\left\langle n\left|\frac{\partial m}{\partial\lambda}\right\rangle =-\epsilon_m\left(\frac{\partial}{\partial\lambda}(\langle n|m\rangle)-\left\langle n\left|\frac{\partial m}{\partial\lambda}\right\rangle\right) -\epsilon_n\left\langle n\left|\frac{\partial m}{\partial\lambda}\right\rangle\right.$$

$$=(\epsilon_m-\epsilon_n)\left\langle n\left|\frac{\partial m}{\partial\lambda}\right\rangle\right. \quad (6)$$

It follows that

$$S_0=-\sum_n{}'\langle m|A|n\rangle\left\langle n\left|\frac{\partial m}{\partial\lambda}\right\rangle\right., \quad (7)$$

or

$$S_0=-\left\langle m\left|A\right|\frac{\partial m}{\partial\lambda}\right\rangle+\langle m|A|m\rangle\left\langle m\left|\frac{\partial m}{\partial\lambda}\right\rangle\right. \quad (8)$$

In a similar fashion

$$S_0'=-\left\langle\frac{\partial m}{\partial\lambda}\right|A\left|m\right\rangle+\langle m|A|m\rangle\left\langle\frac{\partial m}{\partial\lambda}\right|m\right\rangle. \quad (9)$$

Remembering that $\langle m|m\rangle$ is a constant, one obtains

$$S_0+S_0'=-\left(\left\langle m\left|A\right|\frac{\partial m}{\partial\lambda}\right\rangle+\left\langle\frac{\partial m}{\partial\lambda}\right|A\left|m\right\rangle\right), \quad (10)$$

or

$$S_0+S_0'=\left\langle m\left|\frac{\partial A}{\partial\lambda}\right|m\right\rangle-\frac{\partial}{\partial\lambda}(\langle m|A|m\rangle), \quad (11)$$

which completes the proof of (4).

In many second-order perturbation calculations, sums such as (3) occur in which $\Omega\equiv H$, where the Hermitian operator H is the Hamiltonian $H\equiv T+V$, V being a real function. Then one has, from (8), (9), and (11),

$$\sum_n{}' \frac{\langle m|A|n\rangle\langle n|\partial H/\partial\lambda|m\rangle}{E_n-E_m}=-\left\langle m\left|A\right|\frac{\partial m}{\partial\lambda}\right\rangle, \quad (12)$$

$$\sum_n{}' \frac{\langle m|\partial H/\partial\lambda|n\rangle\langle n|A|m\rangle}{E_n-E_m}=-\left\langle\frac{\partial m}{\partial\lambda}\right|A\left|m\right\rangle, \quad (13)$$

$$\sum_n{}' \frac{\langle m|A|n\rangle\langle n|\partial H/\partial\lambda|m\rangle+\langle m|\partial H/\partial\lambda|n\rangle\langle n|A|m\rangle}{E_n-E_m} =\left\langle m\left|\frac{\partial A}{\partial\lambda}\right|m\right\rangle-\frac{\partial}{\partial\lambda}(\langle m|A|m\rangle). \quad (14)$$

Equations (12) and (13) are direct applications of Eqs. (8) and (9), respectively, and of the fact that the eigenfunctions of a real Hamiltonian can always be

[3] Saul T. Epstein, Am. J. Phys. **22**, 613 (1954); W. Byers Brown, Proc. Cambridge Phil. Soc. **54**, 257 (1958).

taken as real[4] ($\langle m|\partial m/\partial\lambda\rangle=\langle\partial m/\partial\lambda|m\rangle=0$). The relations can be used to reduce second-order sums in which occurs the operator $\partial H/\partial\lambda$, or any operator which can be put into the form $\partial H/\partial\lambda$.

The sum-rule, in the form of Eq. (12) for instance, is implicit in Epstein's calculation of the equations of perturbation theory and in Brown's calculation of second-order energy derivatives,[3] in which it is shown that

$$\left|\frac{\partial m}{\partial\lambda}\right\rangle=-\sum_n{}'\frac{\langle n|\partial H/\partial\lambda|m\rangle}{E_n-E_m}\left|n\right\rangle, \tag{15}$$

from which Eq. (12) follows immediately. Brown went on to prove that the general equation for the adiabatic second-order derivative of the energy E_m of an eigenstate $|m\rangle$ with respect to parameters λ and λ' occurring in the Hamiltonian H is

$$\frac{\partial^2E_m}{\partial\lambda\partial\lambda'}=\left\langle m\left|\frac{\partial^2H}{\partial\lambda\partial\lambda'}\right|m\right\rangle -2\sum_n{}'\frac{\langle m|\partial H/\partial\lambda'|n\rangle\langle n|\partial H/\partial\lambda|m\rangle}{E_n-E_m}. \tag{16}$$

Applying the sum-rule (14) to the sum on the right-hand side of this equation, we obtain

$$\frac{\partial^2E_m}{\partial\lambda\partial\lambda'}=\left\langle m\left|\frac{\partial^2H}{\partial\lambda\partial\lambda'}\right|m\right\rangle -\left[\left\langle m\left|\frac{\partial^2H}{\partial\lambda\partial\lambda'}\right|m\right\rangle-\frac{\partial}{\partial\lambda}\left(\left\langle m\left|\frac{\partial H}{\partial\lambda'}\right|m\right\rangle\right)\right] =\frac{\partial}{\partial\lambda}\left(\frac{\partial E_m}{\partial\lambda'}\right),$$

which shows that Eq. (16) and sum-rule (14) are consistent.

Applications of the sum-rule occur in various problems, where it proves extremely useful in the simplification of certain perturbation sums. A first application appears in a subsequent paper,[5] and concerns the Hellmann-Feynman treatment of a spherical atom in a uniform external field; the parameter λ is then equal to the nuclear coordinate. Other simple cases are given below.

3. CASE WHERE λ IS (a) A SCALE FACTOR η, (b) THE MASS M

Consider a system of N particles, with position vectors $\mathbf{r}_1, \cdots\mathbf{r}_i, \cdots\mathbf{r}_N$, and let $\psi_m(\mathbf{r}_i)$ represent a stationary state of the system. If we introduce scaled coordinates $\xi_i=\eta\mathbf{r}_i$,[6] the normalized scaled function is

$$\chi_m(\xi_i,\eta)\equiv\eta^{-3N/2}\psi_m(\xi_i/\eta), \qquad \left(\int\cdots\int\chi_m{}^*\chi_m\cdots d^3\xi_i\cdots=1\right). \tag{17}$$

The Hamiltonian operator H may be written explicitly in terms of the scale factor η as[7]

$$H\equiv T+V =-\eta^2\sum_i\frac{\hbar^2}{2M_i}\frac{\partial}{\partial\xi_i}\cdot\frac{\partial}{\partial\xi_i} +V(\xi_1/\eta,\cdots\xi_i/\eta,\cdots\xi_N/\eta). \tag{18}$$

Hence the partial derivative of H with respect to the parameter η is

$$\frac{\partial H}{\partial\eta}=\frac{2}{\eta}T+\sum_i\frac{\partial V}{\partial(\xi_i/\eta)}\cdot(-\xi_i/\eta^2), \tag{19}$$

or

$$\eta\partial H/\partial\eta=2T-\sum_i\mathbf{r}_i\cdot(\partial V/\partial\mathbf{r}_i). \tag{20}$$

We may now apply our sum-rule, in the form (13) for instance, to the case $\lambda\equiv\eta$,[8] and we obtain

$$\sum_n{}'\frac{\langle m|2T-\sum_i\mathbf{r}_i\cdot(\partial V/\partial\mathbf{r}_i)|n\rangle\langle n|A|m\rangle}{E_n-E_m} =-\eta\left\langle\frac{\partial m}{\partial\eta}\right|A\left|m\right\rangle. \tag{21}$$

In Eq. (21), $|m\rangle$ refers indifferently to ψ_m, with integration over coordinates $\mathbf{r}_i$, or to χ_m, with integration over coordinates ξ_i. This equation is none other than Clinton's sum-rule written in (2). Indeed one has

$$\begin{aligned}\langle m|\sum_i\mathbf{r}_i\cdot\nabla_{(r_i)}(A|m)\rangle &=\sum_i\int\cdots\int\psi_m{}^*\mathbf{r}_i\cdot\nabla_{(r_i)}(A\psi_m)\cdots d^3\boldsymbol{r}_i\cdots\\ &=\sum_i\int\cdots\int\chi_m{}^*\xi_i\cdot\nabla_{(\xi_i)}(A\chi_m)\cdots d^3\xi_i\cdots\\ &=\sum_i\int\cdots\int\nabla_{(\xi_i)}\cdot(\chi_m{}^*\xi_iA\chi_m)\cdots d^3\xi_i\cdots\\ &\quad-\sum_i\int\cdots\int[\nabla_{(\xi_i)}\cdot(\chi_m{}^*\xi_i)]A\chi_m\cdots d^3\xi_i\cdots.\end{aligned} \tag{22}$$

[4] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon Press, New York, 1959), p. 52.

[5] L. Salem and E. B. Wilson, J. Chem. Phys. (to be published).

[6] For an assembly of particles enclosed in a rigid cube of volume L^3, η would be equal to L^{-1}.

[7] W. Byers Brown, J. Chem. Phys. **28**, 522 (1958).

[8] The Hamiltonian operator *is* Hermitian with respect to $\partial\chi/\partial\eta$ [see W. L. Clinton, J. Chem. Phys. (to be published)], so that the derivation of Section 2 is correct and it is allowable to apply the sum-rule to the operator $\partial H/\partial\eta$.

The first integral, which can be transformed into a surface integral by Green's theorem, vanishes because of the nature of χ_m. Hence

$$\langle m|\sum_i \mathbf{r}_i\cdot\nabla_{(r_i)}(A|m)\rangle$$
$$=-\sum_i 3\int\cdots\int\chi_m^*A\chi_m\cdots d^3\xi_i\cdots$$
$$-\sum_i\int\cdots\int\xi_i\cdot(\nabla_{(\xi_i)}\chi_m^*)A\chi_m\cdots d^3\xi_i\cdots. \quad (23)$$

Using the relation

$$\eta\partial\chi_m/\partial\eta=-\tfrac{3}{2}N\chi_m-\textstyle\sum_i\xi_i\partial\chi_m/\partial\xi_i \quad (24)$$

to calculate the second integral on the right-hand side of (23), we obtain

$$\langle m|\sum_i \mathbf{r}_i\cdot\nabla_{(r_i)}(A|m)\rangle+\tfrac{3}{2}N\langle m|A|m\rangle$$
$$=\eta\langle\partial m/\partial\eta|A|m\rangle, \quad (25)$$

which proves our contention. It follows that Clinton's sum-rule is in fact a particular case of the more general relation derived in paragraph 2.

If V is an electrostatic Coulombic potential, and hence a homogeneous function of the coordinates of degree -1, Eq. (21) becomes

$$\sum_n{}'\frac{\langle m|T|n\rangle\langle n|A|m\rangle}{E_n-E_m}=-\eta\left\langle\frac{\partial m}{\partial\eta}\middle|A\middle|m\right\rangle. \quad (26)$$

However an independent expression can be obtained for the left-hand side of Eq. (26). Assuming, for convenience, the mass of all the particles to be the same and equal to M, we have

$$T=(1/M)[\partial H/\partial(1/M)], \quad (27)$$

so that the sum-rule (13) applied to the case $\lambda\equiv 1/M$ yields

$$\sum_n{}'\frac{\langle m|T|n\rangle\langle n|A|m\rangle}{E_n-E_m}=-\frac{1}{M}\left\langle\frac{\partial m}{\partial(1/M)}\middle|A\middle|m\right\rangle. \quad (28)$$

It follows from (26) and (28) that χ_m must obey the differential equation[9]

$$\frac{1}{M}\frac{\partial\chi_m}{\partial(1/M)}=\eta\frac{\partial\chi_m}{\partial\eta}, \quad (29)$$

or, using (24),

$$\frac{1}{M}\frac{\partial\chi_m}{\partial(1/M)}=-\tfrac{3}{2}N\chi_m-\sum_i\xi_i\frac{\partial\chi_m}{\partial\xi_i}. \quad (30)$$

Hence

$$\frac{1}{M}\frac{\partial\psi_m}{\partial(1/M)}=-\tfrac{3}{2}N\psi_m-\sum_i\mathbf{r}_i\frac{\partial\psi_m}{\partial\mathbf{r}_i}. \quad (31)$$

Equation (31) will hold for any eigenfunction ψ_m of a Hamiltonian $H\equiv T+V$, where V is a Coulombic potential. It may be easily verified, for instance, in the case of the ground-state wave function of the hydrogen atom. Consequences of this relation have been studied in detail by Clinton.[2]

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[9] Professor E. B. Wilson has kindly pointed out to the author that Eq. (29) can be obtained directly by introducing dimensionless variables into the Schrödinger equation; for the hydrogen atom for instance, the dimensionless equation $-\frac{1}{2}\nabla^2_{(\mathbf{r})}\psi-(1/r)=\epsilon\psi$, admits the familiar solution $\psi(r)=\pi^{-\frac{1}{2}}\exp(-r)$. If, however, we had kept variables with dimensions, $\xi=a_0r$ and $E=(e^2/a_0)\epsilon$, the corresponding equation,

$$-(h^2/8\pi^2M)\nabla^2_{(\xi)}\chi-(e^2/\xi)\chi=E\chi,$$

would have yielded a solution $\chi(\xi,a_0)=\pi^{-\frac{1}{2}}a_0^{-\frac{3}{2}}\exp(-\xi/a_0)\equiv a_0^{-\frac{3}{2}}\psi(\xi/a_0)$. Comparing with (17) we see that a_0, when it appears explicitly, behaves exactly like a scale factor η. Hence $a_0\partial\chi/\partial a_0=\eta\partial\chi/\partial\eta$ and, since by definition $a_0=[h^2/(4\pi^2e^2)](1/M)$, Eq. (29) follows.