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Weak Interactions in Molecular Quantum Mechanics

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WEAK interaction terms in the many-body Hamiltonian are of considerable interest to molecular quantum mechanics. Because of their small magnitude, they are usually ignored in the determination of electronic wave functions. The detailed interpretation of the interaction terms shows, however, that they can be utilized both for the quantitative appraisal of approximate wave functions and for the qualitative verification of theoretical constructs. In this paper, we first outline perturbation methods that can be used for the calculation of the weak interactions and then give an indication of their importance to molecular theory by a discussion of certain applications.

In most attempts to approximate the electronic wave functions of simple molecules, such as those reported at this Conference, a Hamiltonian operator of the form

$$\mathcal{H}_0 = T_e + V \tag{1}$$

has been used. Here T_e represents the kinetic energy of the electrons and V the Coulomb energy of the electrons and nuclei regarded as point charges. As is well known, the complete electronic Hamiltonian contains a large number of additional terms. Some of these, such as the electron-coupled nuclear-spin interactions and the nuclear quadrupole coupling are due to the fact that neither the electrons nor the nuclei can be completely described by the point charge model used in Eq. (1). Other terms arise from the interaction between electronic and nuclear motion. In the presence of external electric and magnetic fields, still more terms have to be included. All of these additional terms, which comprise the weak interactions in molecules, have in common that their contribution to the electronic energy is generally a small part of the total. In comparison with the Hamiltonian of Eq. (1), which involves energies on the order of electron volts, the weak interactions are usually in the range 10^{-4} to 10^{-14} ev. In spite of their small magnitude, the weak interactions often can be measured to a very high accuracy by a number of methods, such as microwave, magnetic resonance, and electric resonance spectroscopy.

PERTURBATION THEORY APPROACH

To permit a fruitful comparison of the experimental measurements and molecular theory, a technique must be available for the evaluation of the weak interaction terms from approximate electronic wave functions. Because of the minute effects of the weak interactions, perturbation theory is ideally suited for the purpose. We write the Hamiltonian $\mathcal{H}$ for a system in the usual form

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}', \tag{2}$$

where $\mathcal{H}_0$ is given by Eq. (1) and $\mathcal{H}'$ is the operator required for the particular weak interaction that is being considered. If the exact zero-order functions $\Psi_n{}^0$ and energies $E_n{}^0$ that satisfy the equation

$$\mathcal{H}_0 \Psi_n{}^0 = E_n{}^0 \Psi_n{}^0 \tag{3}$$

are known, the perturbation energy ΔE for the ground state of the molecule is given by the expression

$$\Delta E = \langle \Psi_0{}^0 | P | \Psi_0{}^0 \rangle, \tag{4}$$

where P is the perturbation operator. In general, P has the form

$$P = \sum_l P_l = \mathcal{H}' + \mathcal{H}' \left\{ \sum_{n \neq 0} \frac{|\Psi_n{}^0\rangle \langle \Psi_n{}^0|}{E_0{}^0 - E_n{}^0} \right\} \mathcal{H}' + \cdots. \tag{5}$$

For most problems involving weak interactions, only the first two terms in Eq. (5) are of interest. By substituting these terms into Eq. (4), we have the first-order energy $\Delta E_0{}^1$,

$$\Delta E_0{}^1 = \langle \Psi_0{}^0 | P_1 | \Psi_0{}^0 \rangle = \langle \Psi_0{}^0 | \mathcal{H}' | \Psi_0{}^0 \rangle, \tag{6}$$

and the second-order energy $\Delta E_0{}^2$,

$$\Delta E_0{}^2 = \langle \Psi_0{}^0 | P_2 | \Psi_0{}^0 \rangle = \sum_{n \neq 0} \frac{\langle \Psi_0{}^0 | \mathcal{H}' | \Psi_n{}^0 \rangle \langle \Psi_n{}^0 | \mathcal{H}' | \Psi_0{}^0 \rangle}{E_0{}^0 - E_n{}^0}. \tag{7}$$

Although Eqs. (6) and (7) provide formal expressions for the desired quantities, lack of knowledge of exact values for $\Psi_n{}^0$ and $E_n{}^0$ raises problems in their application. Fortunately, there is no need to have an exact value of $E_0{}^0$ for $\Delta E_0{}^1$, since the first-order energy is calculated directly rather than from the difference in the total energy. For $\Delta E_0{}^2$, one does require values for the zero-order energies so as to be able to obtain the energy denominator $(E_0{}^0 - E_n{}^0)$ in Eq. (7). A greater difficulty with Eq. (7) is that although reasonable approximations to the ground-state wave functions are available for a few simple molecules, very little is known about the excited states. The few attempts that have been made to evaluate $\Delta E_0{}^2$ by summing over a selected finite set of approximate excited-state functions are confused by the question of the importance of the continuum contributions. These com-

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plications suggest that some procedure for avoiding the need for the excited-state functions in ΔE_0^2 is essential.

Two methods that reduce the problem of evaluating ΔE_0^2 to one involving only the ground-state function Ψ_0^0 have been introduced. The first of these makes use of a matrix sum rule to obtain the equation

$$P_2 = -\mathcal{H}'(\mathcal{H}' - \Delta E_0^1)/\Delta, \tag{8}$$

where Δ is the so-called average excitation energy, which is formally defined as the quantity required to make Eq. (8) exact. To avoid the necessity for solving Eq. (8) for Δ, which would reintroduce the summation problems that we are trying to avoid, a semitheoretical estimate of Δ can be made. This is commonly done by using the form of $\mathcal{H}'$ to determine the excited states that make the most important contribution to P_2 and then attempting to relate a guess at their energy spacing to a likely value of Δ. Although there are obvious difficulties in finding an accurate Δ by such a crude procedure, the values obtained should generally be within a factor of two of the correct result and in favorable cases considerably closer than that. If all the terms in P_2 result in contributions to ΔE_0^2 of the same sign, an upper limit to the perturbation energy can be found by an appropriate choice of Δ.

The second method, which is considerably more reliable than the use of a Δ value, introduces a function Φ such that

$$P_2 = (\mathcal{H}' - \Delta E_0^1)\Phi, \tag{9}$$

where the function Φ is obtained by solving the first-order perturbation equation

$$(E_0^0 - \mathcal{H}_0)\Phi\Psi_0^0 = (\mathcal{H}' - \Delta E_0^1)\Psi_0^0. \tag{10}$$

This method might be called the differential equation approach. In some cases, particularly those arising in atomic systems, Eq. (10) can be reduced to a one-dimensional problem for which a direct numerical integration is feasible. Since such a simplification is usually not possible for molecules, another procedure, such as the variation method, must be used to determine Φ from Eq. (10). Equation (10) assumes that the function Ψ_0^0 is an exact solution of the zero-order equation [Eq. (3)]. For molecular problems, in which this assumption is violated by the approximate functions that are available, one can use the device of constructing an effective unperturbed Hamiltonian $\mathcal{H}_0^{\mathrm{ef}}$ to replace $\mathcal{H}_0$ in Eqs. (3) and (10). $\mathcal{H}_0^{\mathrm{ef}}$ is given by

$$\mathcal{H}_0^{\mathrm{ef}} = T_e + V^{\mathrm{ef}}, \tag{11}$$

where

$$(V^{\mathrm{ef}} - E_0^0) = -(T_e\Psi_0^0/\Psi_0^0). \tag{12}$$

If a Hartree-Fock solution has been obtained for the zero-order Hamiltonian, the Hartree-Fock operator can be used directly in the set of coupled one-electron equations that appear instead of Eq. (10).

Both the average excitation energy approach [Eq. (8)] and the differential equation approach [Eq. (9)] are applicable to calculations of weak interactions in molecules. By their use, the second-order contributions ΔE_0^2, as well as the first-order energy ΔE_0^1, has been expressed in a form that requires only the ground-state solution of Eq. (1). In the following sections, these formulations for the determination of weak interactions from a knowledge of approximate wave functions are applied to problems of molecular theory.

Early theoretical studies in the area of weak interactions were made by Unsöld,[1] Van Vleck and Frank,[2] Lennard-Jones,[3] Hasse,[4] Slater and Kirkwood,[5] and Buckingham.[6] The recent refinements in the experimental techniques for the measurement of weak interactions have stimulated a renewed interest in their calculation. Some of the workers involved are Sternheimer (nuclear quadrupole coupling in atoms and ions),[7] Tillieu and Guy (electric and magnetic susceptibilities),[8] Dalgarno et al. (polarizabilities in atoms),[9] Das and Bersohn (magnetic shielding in molecules),[10] Stephens (magnetic shielding and spin coupling in molecules),[11] and Ishiguro et al. (accurate wave functions for weak interactions in H_2).[12]

APPRAISAL OF APPROXIMATE WAVE FUNCTIONS

We now show how the theory of weak interactions can be used to appraise approximate wave functions. By means of the differential equation approach to ΔE_0^2, both the first-order and the second-order contributions to the weak interactions can be calculated by perturbation theory. The accuracy of the method is such that any difference between the calculated results and the experimental measurements should be due to errors in the wave function. Since certain of the weak interactions involve operators whose major contributions come from regions of space different from those emphasized by the Hamiltonian of Eq. (1), an examination of the results obtained with a number of these

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[1] A. Unsöld, Ann. Physik **82,** 380 (1927).

[2] J. H. Van Vleck and A. Frank, Proc. Natl. Acad. Sci. U.S. **15,** 539 (1929).

[3] J. E. Lennard-Jones, Proc. Roy. Soc. (London) **A129,** 598 (1930).

[4] H. R. Hasse, Proc. Cambridge Phil. Soc. **26,** 542 (1930).

[5] J. C. Slater and J. G. Kirkwood, Phys. Rev. **37,** 682 (1931).

[6] R. A. Buckingham, Proc. Roy. Soc. (London) **A160,** 94 (1937).

[7] R. M. Sternheimer, Phys. Rev. **80,** 102 (1950); see also H. M. Foley, R. M. Sternheimer, and D. Tycko, ibid. **93,** 734 (1954) and more recent papers in *The Physical Review.*

[8] J. Tillien and G. Guy, Compt. rend. **239,** 1203 (1954), **240,** 1402 (1955); also J. Guy and M. Harrand, ibid. **234,** 616 (1952).

[9] (a) T. P. Das and R. Bersohn, Phys. Rev. **104,** 849L (1956); (b) **102,** 733 (1956).

[10] A. Dalgarno and A. L. Stewart, Proc. Roy. Soc. (London) **A238,** 269 (1956); **A247,** 245 (1958), and other papers in the *Proceedings of the Royal Society* (*London*), Series A.

[11] M. J. Stephens, Proc. Roy. Soc. (London) **A243,** 264, 274 (1958).

[12] E. Ishiguro, T. Arai, M. Mizushima, and M. Kotani, Proc. Phys. Soc. (London) **A65,** 178 (1952); E. Ishiguro and S. Koide, Phys. Rev. **94,** 350 (1954); E. Ishiguro, ibid. **111,** 203 (1958).

Table I. Magnetic susceptibility and shielding in H_2[a] (ΔE_0^1 terms).

	$\langle x^2\rangle$ (A^2)	$\langle z^2\rangle$ (A^2)	$\langle z^2-x^2\rangle$ (A^2)	$\langle\chi^d\rangle$ (10^{-6} emu)	$\langle\sigma^d\rangle$ (10^{-5})
Experiment[b]	0.214	0.297	0.083	4.11	3.15
Heitler-London ($Z=1$) function	0.291	0.398	0.108	5.55	2.84
Wang ($Z=1.16$) function	0.216	0.328	0.112	4.30	2.96
LCAO-MO ($Z=1.193$) function	0.208	0.310	0.102	4.17	3.08
Nordsieck function	0.210	0.297	0.081	4.02	3.24

[a] M. Karplus, J. Chem. Phys. **25**, 605 (1956), and unpublished calculations.

[b] See reference 13.

interactions provides a much more detailed experimental test of the wave function than does the energy criterion alone.

To illustrate the approach, we consider some properties of the hydrogen molecule, for which the most accurate experimental and theoretical results are available. Of the large number of weak interactions that have been studied in H_2, we restrict ourselves to the molecular magnetic susceptibility and the proton magnetic shielding. These two interactions are of special interest because the refined molecular beam techniques of Ramsey and his co-workers[13] have made possible a separate experimental evaluation of the ΔE_0^1 and ΔE_0^2 contributions to the perturbation energy.

For the first-order (diamagnetic) terms in $'\Sigma$ molecules, the energy corresponding to the susceptibility χ is given by

$$\Delta E_0^1(\chi)=\langle\Psi_0^0\mid\tfrac{1}{2}H_\alpha\chi_{\alpha\beta}^dH_\beta\mid\Psi_0^0\rangle, \qquad (13)$$

and that corresponding to the shielding σ by

$$\Delta E_0^1(\sigma)=\langle\Psi_0^0\mid\mu_\alpha\sigma_{\alpha\beta}^dH_\beta\mid\Psi_0^0\rangle. \qquad (14)$$

Here H_α and μ_α are the α components of the magnetic field and proton moment, respectively, $\chi_{\alpha\beta}^d$ is a component of the diamagnetic part of the susceptibility tensor given by

$$\chi_{\alpha\beta}^d=(e^2/8mc^2)\sum_i(\delta_{\alpha\beta}r_i^2-x_{i\alpha}x_{i\beta}), \qquad (15)$$

and $\sigma_{\alpha\beta}^d$ is a component of the diamagnetic part of the shielding tensor given by

$$\sigma_{\alpha\beta}^d=(e/2mc)^2\sum_i[(\delta_{\alpha\beta}r_i^2-x_{i\alpha}x_{i\beta})/r_i^3]. \qquad (16)$$

The cylindrical symmetry of H_2 reduces to two the number of independent components of these tensors; with the molecular axis in the z direction, we have to determine $\langle\chi_{xx}^d\rangle=\langle\chi_{yy}^d\rangle$, $\langle\chi_{zz}^d\rangle$ and $\langle\sigma_{xx}^d\rangle=\langle\sigma_{yy}^d\rangle$, $\langle\sigma_{zz}^d\rangle$. For the susceptibility, the individual components have been determined separately by their dependence on the quantum number m_J. A comparable separation of the components of the shielding tensor should be possible; however, the required experimental accuracy has as yet not been attained.[14] In Table I, we list the second moments of the charge distribution $\langle x^2\rangle=\langle y^2\rangle$, $\langle z^2\rangle$, and $\langle z^2-x^2\rangle$, which are obtained directly from the corresponding $\langle\chi_{\alpha\alpha}^d\rangle$ values, and $\langle\chi^d\rangle$ and $\langle\sigma^d\rangle$, which are rotational averages of the tensors; i.e., $\langle\chi^d\rangle=\frac{2}{3}\langle\chi_{xx}^d\rangle+\frac{1}{3}\langle\chi_{zz}^d\rangle$ and $\langle\sigma^d\rangle=\frac{2}{3}\langle\sigma_{xx}^d\rangle+\frac{1}{3}\langle\sigma_{zz}^d\rangle$. Table I also lists the values for these quantities calculated with certain of the simpler approximate wave functions for H_2. The particular functions chosen are those which have been determined for a number of internuclear distances so as to permit averaging over the zero-point vibrations. Comparison of the experimental and theoretical results shows very clearly that the rather poor results obtained with the Heitler-London function are considerably improved in the Wang and LCAO-MO functions. The introduction of an effective charge parameter contracts the charge distribution to nearly the correct "size" as measured by both the susceptibility terms (which vary as r^2) and the shielding term (which varies as r^{-1}). For a good value of the quadrupole moment ($\langle z^2\rangle-\langle x^2\rangle$), there is necessary the additional flexibility in "shape" that is provided by the Nordsieck function. When the calculated values of $\langle x^2\rangle$ and $\langle z^2\rangle$ for the 28-term James and Coolidge type function (reported by Kolos and Roothaan at this Conference) are averaged over an empirical vibrational potential, exact agreement between theory and experiment is obtained. By contrast, their 9-term SCF function yields the values $\langle x^2\rangle=0.219A^2$ and $\langle z^2\rangle=0.297A^2$, the first of which is not quite correct.

For the second-order (paramagnetic) terms, the energy expressions have the same general form as the first-order contributions; that is,

$$\Delta E_0^2(\chi)=\langle\Psi_0^0\mid\tfrac{1}{2}H_\alpha\chi_{\alpha\beta}^pH_\beta\mid\Psi_0^0\rangle, \qquad (17)$$

and

$$\Delta E_0^2(\sigma)=\langle\Psi_0^0\mid\mu_\alpha\sigma_{\alpha\beta}^pH_\beta\mid\Psi_0^0\rangle. \qquad (18)$$

The expressions for the operators, however, are considerably more complicated than their first-order counterparts. For the components of the paramagnetic susceptibility tensor, we have

$$\chi_{\alpha\beta}^p=-(e/2mc)^2\sum_i m_{i\alpha}\left\{\sum_{n\neq0}\frac{|\Psi_n^0\rangle\langle\Psi_n^0|}{E_0^0-E_n^0}\right\}\sum_j m_{j\beta}, \qquad (19)$$

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[13] N. F. Ramsey, *Molecular Beams* (Clarendon Press, Oxford, England, 1956).

[14] N. F. Ramsey (private communication).

Table II. Magnetic susceptibility and shielding in H_2. (ΔE_0^2 and $\Delta E_0=\Delta E_0^1+\Delta E_0^2$ terms).

	$\langle\chi_{xx}^p\rangle$[a] ($10^{-6}$ emu)	$\langle\sigma_{xx}^p\rangle$[b] ($10^{-5}$)	$\langle\chi\rangle$[a] (10^{-6} emu)	$\langle\sigma\rangle$[b] (10^{-5})
Experiment[c]	−0.0846	−0.63	4.03	2.52
Heitler-London ($Z=1$) function	−0.465	−0.39	5.08	2.45
Wang ($Z=1.16$) function	−0.334	−0.50	3.97	2.46
LCAO–MO ($Z=1.19$) function	−0.289	−0.54	3.88	2.54
Nordsieck function	−0.106	...	3.91	...

[a] J. Tillien and G. Guy, see reference 8; J. Chem. Phys. **24,** 1117 (1956); I. Espe, Phys. Rev. **103,** 1254 (1956).
[b] See references 9(a) and 11, p. 264.
[c] See reference 13.

and for the components of the paramagnetic shielding tensor,

$$\sigma_{\alpha\beta}^p=-2(e/2mc)^2\left[\sum_i m_{i\alpha}\left\{\sum_{n\neq 0}\frac{|\Psi_n^0\rangle\langle\Psi_n^0|}{E_0^0-E_n^0}\right\}\sum_j(m_{j\beta}/r_j^3)+\text{complex conjugate}\right], \quad (20)$$

where $m_{i\alpha}$ is the α component of the angular momentum operator for electron i. With the molecular axis in the z direction, the only nonzero contributions to the tensors come from $\langle\chi_{xx}^p\rangle=\langle\chi_{yy}^p\rangle$ and $\langle\sigma_{xx}^p\rangle=\langle\sigma_{yy}^p\rangle$. Experimental and theoretical values for these quantities are given in Table II. The agreement for the second-order terms is considerably worse than that found for the first-order contributions. This result is not surprising since the angular momentum operators involved in the P_2 terms of Eqs. (19) and (20) introduce derivatives, which serve as a considerably more sensitive test of the form of wave functions than do the operators of Eqs. (15) and (16). Just as for the diamagnetic terms, some improvement is found on introducing an effective charge parameter. However, only when the Nordsieck function is used does one approach the correct result for $\langle\chi_{xx}^p\rangle$; no comparable calculation is available for $\langle\sigma_{xx}^p\rangle$. From the viewpoint of the calculation of experimental quantities, it is of interest that the total suceptibility and shielding constants are obtained in very good agreement with the measured values because of the small contribution made by the paramagnetic terms and their errors (Table II).[15]

Thus we see that the magnetic susceptibility and shielding (especially the second-order terms) provide a considerable challenge for approximate wave functions. Although comparable information from weak interaction measurements has been obtained for molecules other than hydrogen, relatively little use has been made of it, even in the cases where wave functions are available. In Table III, we give some preliminary results from a study of H_2O and NH_3. The $\langle r^2\rangle$ values determined from the diamagnetic part of the susceptibility are compared with the theoretical results calculated from the SCF-LCAO-MO wave function of Ellison and Shull[16] for H_2O and Higuchi[17] for NH_3. Although no flexibility in the effective charge parameters of the hydrogen orbitals was introduced into the wave function, the agreement between experiment and theory is quite good. No results for the paramagnetic terms are available.[18]

Table III. Magnetic susceptibility of polyatomic molecules (ΔE_0^1 terms).

	$\langle r^2\rangle_{\text{calc}}$ (A^2)	$\langle r^2\rangle_{\text{exptl.}}$ (A^2)	$\langle\chi^d\rangle_{\text{calc}}$ (10^{-6} emu)	$\langle\chi^d\rangle_{\text{exptl.}}$ (10^{-6} emu)
H_2O	0.51	0.56[a]	14.4	15.9[a]
NH_3	0.79	0.81[b]	22.4	22.9[b]

[a] R. F. Schwarz, thesis, Harvard University, 1952.
[b] J. R. Eshbach and M. W. P. Strandberg, Phys. Rev. **85,** 24 (1952).

For systems with unpaired spins in doublet or triplet states, a number of first-order weak interactions have been measured that are not observed in singlet species. Detailed studies of these interactions have been made by microwave methods in a few stable molecules such as NO and O_2. In spite of extensive attempts to find unstable gas phase radicals, the only successful experiments have been done with OH. It seems likely that microwave and paramagnetic resonance spectroscopy will soon increase the number of molecules for which data are available. To illustrate briefly the type of results that are obtained, we list in Table IV certain of the operators that occur. The $\langle 1/r^3\rangle$ interaction arises from spin-orbit coupling in states of nonzero orbital angular momentum. Both the $\langle\sin^2\theta/r^3\rangle$ and the $\langle(3\cos^2\theta-1)/r^3\rangle$ terms are obtained from hyperfine interactions between the electron-spin and the nuclear-spin magnetic dipoles. For triplet states, the spin dipole-dipole coupling between a pair of electrons leads to the

$$\langle(3\cos^2\theta_{12}-1)/r_{12}^3\rangle$$

term. Numerical values for these interactions in NO, O_2, and OH are given in Table IV, with theoretical estimates of their magnitude made from approximate wave functions determined by the variational method. The listed experimental results depend on the particular model used for the interpretation of the microwave spectra; in both NO and OH, additional work is

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[15] For a more general and detailed discussion of the properties of the hydrogen molecule, see T. P. Das and R. Bersohn, Phys. Rev. **115,** 897 (1959).

[16] F. O. Ellison and H. Shull, J. Chem. Phys. **23,** 2348 (1955).

[17] J. Higuchi, J. Chem. Phys. **24,** 535 (1956).

[18] Dr. T. D. Das has kindly informed me that he has calculated $\langle\chi^p\rangle$ for H_2O from a localized orbital wave function. The result obtained is much smaller than the experimental value of 1.46×10^{-6} emu.

TABLE IV. Interactions in simple nonsinglet species ($\Delta E_0{}^1$ terms).

(Units of 10^{24} cm^3)	$\langle 1/r^3 \rangle$	$\langle \sin^2\theta)/r^3 \rangle$	$\langle (3\cos^2\theta - 1)/r^3 \rangle$	$\Psi^2(0)$	$\langle (3\cos^2\theta_{12}{}^{-1})/r_{12}{}^3 \rangle$[a]
N^{14} O					
Exptl.[b]	14.6	13.4	−11.8	1.02	
Calc[c]	16.7	13.2	−6.2	...	
O O^{17}					
Exptl.[d]			−19.8	1.26	18.3
Calc (Kotani)[e]			−11.6	1.31	...
Calc (Meckler)[f]			−16.3	...	10.8
O H^1					
Exptl.[g]	(0.75)	(0.49)			
Calc[h]	0.95	0.27			

[a] Includes Coulomb and exchange terms.

[b] M. Mizushima, Phys. Rev. **105**, 1262 (1957), and earlier references therein.

[c] Estimated from the wave function of H. Brion, C. Moser, and M. Yamazaki, J. Chem. Phys. **30**, 673 (1959). Hartree-Fock values for atomic $\langle 1/r^3 \rangle$ terms were used.

[d] M. Tinkam and M. W. P. Strandberg, Phys. Rev. **97**, 937 (1955); S. L. Miller and C. H. Townes, ibid. **90**, 537 (1953).

[e] M. Kotani, Y. Mizuno, K. Kayama, and E. Ishiguro, J. Phys. Soc. Japan, **12**, 707 (1957).

[f] Calculated by Tinkam and Strandberg (reference d) from the wave function of A. Meckler, J. Chem. Phys. **21**, 1750 (1953).

[g] G. C. Dousmanis, T. M. Sanders, Jr., and C. H. Townes, Phys. Rev. **100**, 1735 (1955).

[h] Estimated from the wave function of M. Krauss, J. Chem. Phys. **29**, 1287 (1958).

required to clarify the interactions involved. Comparison of the calculated and the measured values shows reasonable agreement for most of the one-electron quantities. Without much additional refinement in the wave functions for these diatomic molecules, quite accurate values should be attainable. The two-electron interaction in O_2 is more sensitive to the detailed form of the wave function. Since this interaction offers a direct approach to electron correlation, it is of considerable interest to molecular theory and should be carefully examined in system other than O_2. The recent study of the excited triplet state in naphthalene by paramagnetic resonance[19] demonstrates the wider applicability of this approach to the correlation problem.

VERIFICATION OF THEORETICAL CONSTRUCTS

In the usual form of valence theory, a large number of constructs are used for the description of the electronic structure of molecules. Since many of these constructs, such as $\sigma-\pi$ interaction, hybridization, and hyperconjugation, have been introduced in the explanation of only small differences in the total energy of molecules, it has usually been difficult to obtain reliable criteria for estimating their contribution. We now wish to show how the weak interactions involved in the electron coupling of nuclear spins can be used as a measure for the deviations from perfect pairing that are involved in hyperconjugation. In the nuclear magnetic resonance spectra of rapidly reorienting molecules, pairs of nuclear spins $\mathbf{I}_N$ and $\mathbf{I}_{N'}$ interact through a second-order process to yield an energy $\Delta E_0{}^2(a_{NN'})$ of the form

$$\Delta E_0{}^2(a_{NN'}) = \langle \Psi_0{}^0 \,|\, \mathbf{I}_N \cdot a_{NN'} \cdot \mathbf{I}_{N'} \,|\, \Psi_0{}^0 \rangle, \qquad (21)$$

where the expectation value of the operator $a_{NN'}$ is the coupling constant $A_{NN'}$; that is, $A_{NN'} = \langle a_{NN'} \rangle$. To a good approximation, the coupling operator for a pair of protons $a_{HH'}$ can be written

$$a_{HH'} = (2/3h)(16\pi\beta\hbar/3)^2 \gamma_H{}^2 \Big(\sum_k \delta(\mathbf{r}_{KH})\mathbf{S}_k\Big) \cdot \left\{ \sum_{n\neq 0} \frac{|\Psi_n{}^0\rangle\langle\Psi_n{}^0|}{E_0{}^0 - E_n{}^0} \right\} \Big(\sum_l \delta(\mathbf{r}_{lH'})\mathbf{S}_l\Big), \qquad (22)$$

where $\mathbf{S}_k$ represents the spin operator (in units of $\hbar$) and β, γ_H, etc. correspond to standard notation. By means of the average excitation energy method [Eq. (8)], we can reduce Eq. (22) to the form

$$a_{HH'} = -(2/3h\Delta)(16\pi\beta\hbar/3)^2 \cdot \gamma_H{}^2 \Big(\sum_{k,l} \delta(\mathbf{r}_{kH})\delta(\mathbf{r}_{lH'})\mathbf{S}_k \cdot \mathbf{S}_l\Big), \qquad (23)$$

since $\Delta E_0{}^1$ is zero in this case. By using Eq. (23) for $a_{HH'}$ and expanding the ground-state wave function $\Psi_0{}^0$ in terms of a set of canonical valence-bond singlet structures $\Psi_r{}^0$, we find that $A_{HH'}$ in cps is equal to the expression[20]

$$A_{HH'} = (6h\Delta)^{-1}(16\pi\beta h/3)^2 \gamma_H{}^2 \phi_H(0)\phi_{H'}(0) \cdot \sum_{r,s} c_r c_s (2^{n-i_{rs}})^{-1}[1 + 2f_{rs}(P_{HH'})], \qquad (24)$$

where c_r is the coefficient for contribution of $\psi_r{}^0$ to $\Psi_0{}^0$, $2n$ is the number of electrons, i_{rs} is the number of islands in the superposition diagram for structures r and s, $\phi_H(0)$ and $\phi_{H'}(0)$ represent the electron density at nuclei H and H', respectively, and $f_{rs}(P_{HH'})$ is the exchange factor for orbital H and H' in the (rs) superposition diagram. From the form of Eq. (24) and the

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[19] C. A. Hutchison and B. W. Magnum, J. Chem. Phys. **29**, 952 (1958); see also the theoretical interpretation by M. Gouterman, J. Chem. Phys. **30**, 1369 (1959).

[20] M. Karplus and D. H. Anderson, J. Chem. Phys. **30**, 6 (1959).

meaning of the exchange factor in valence-bond theory, it is evident that if H and H' cannot be represented as bonded together in any of the structures with a nonzero coefficient $[f_{rs}(p_{HH'})=-\frac{1}{2}$ for all r, $s]$, $A_{HH'}$ is equal to zero. Conversely, for chemically nonbonded atoms, a value of $A_{HH'}$ different from zero implies that structures other than the perfect pairing structure contribute to the ground-state wave function.

Applying this approach to the ethane molecule, we have calculated the coupling constant for a pair of protons attached to different carbon atoms. Contributions to Ψ_0^0 of all the possible nonionic structures χ_r in the HCC′H′ fragment model of ethane were evalued by standard variational techniques, Δ was set equal to twice the C—H bond energy, and $\phi_H(0)$, $\phi_{H'}(0)$ were obtained from hydrogen atom wave functions. The resulting expression for $A_{HH'}$ as a function of the dihedral angle ϕ between the HCC′ and CC′H′ plane is given approximately by the equation[21]

$$A_{NN'}=\begin{Bmatrix} 8.5\cos^2\phi-0.28 & 0\leq\phi\leq 90^{0} \\ \\ 9.5\cos^2\phi-0.28 & 90^{\circ}\leq\phi\leq 180^{\circ}\end{Bmatrix}. \qquad (25)$$

Experiments by a number of workers[22] have shown that the form of Eq. (25) is correct, although the coefficients of the $\cos^2\theta$ terms are probably in the neighborhood of 12 and 14 instead of the theoretical values of 8.5 and 9.5, respectively. Since H and H' are not bonded together in the perfect pairing structure, these values for the coupling constant provide direct evidence for the occurrence of deviations from perfect pairing in ethane. Using the valence-bond calculations, we find that the additional structures contribute 3.18 kcal of “hyperconjugation energy to the ground state. Although this value is probably not exact, the general agreement between the coupling-constant theory and experiment indicates that it is of the correct order of magnitude. Similar results have been found for a number of systems.[21,23] Further, if the coupling constants for atoms other than hydrogen are considered, information concerning orbital hybridization and bond polarization can be obtained.[24]

CONCLUSION

We have tried to demonstrate that the study of weak interactions can play an important role in molecular theory. When formulated in terms of perturbation theory, they can be of considerable utility in the analysis of electronic wave function. Now that there are a number of groups actively engaged in the determination of approximate wave functions by automatic high-speed computer methods, an increased concern with weak-interaction measurements is to be expected.

From the results available at present, it seems that quite accurate theoretical values for at least some of the weak interactions are within the range of possibility. To obtain such reliable values, it will be necessary to consider the form of the weak-interaction operator that is being calculated and to introduce the appropriate flexibility into the approximate wave function. The magnitudes determined for the weak interactions by such a careful approach should then be of sufficient accuracy to aid in the interpretation of microwave and radio-frequency spectra.

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