PHYSICAL REVIEW
LETTERS

VOLUME 23 1 SEPTEMBER 1969 NUMBER 9

MANY-BODY PERTURBATION THEORY APPLIED TO MOLECULES*

H. P. Kelly
Department of Physics, University of Virginia, Charlottesville, Virginia 22903

(Received 23 June 1969)

A method for applying many-body perturbation theory to molecules is discussed. The energy of H_2 is calculated to be -1.176 a.u. Results are also given for the static dipole polarizability.

Methods for applying the many-body perturbation theory of Brueckner[1] and Goldstone[2] to atoms have been discussed previously.[3] For atoms one calculates a complete set of single-particle states in a spherically symmetric potential. The many-body theory[1,2] is applicable also to molecules, but one might expect greater difficulty in generating an appropriate complete set of single-particle states because of the lack of spherical symmetry. The most successful methods for obtaining molecular orbitals have been reviewed, for example, by Slater.[4]

In this paper we start by calculating single-particle states for H_2 about the center of the molecule. This gives only a rough approximation to the correct molecular orbitals, and we use perturbation theory to correct our initial crude approximation. Since we use a spherically symmetric potential, we readily obtain a complete set of single-particle states as in the atomic case.[3]

For H_2, the interaction of an electron with the nuclei is given by

$$-\sum_k \frac{2r_<^k}{r_>^{k+1}} P_k(\cos\theta), \tag{1}$$

where $r_<$ is the lesser of r, the electron distance from the origin, and $R=0.70$, which is one-half the nuclear separation.[5]

In this calculation, the single-particle states are calculated by the Schrödinger equation with

$$V(r) = \frac{-2}{r_>} + \int d\vec{r}' \frac{|\varphi_{1s}'(\vec{r}')|^2}{|\vec{r}-\vec{r}'|}, \tag{2}$$

where φ_{1s}' is an approximation (spherically averaged) to the lowest molecular orbital. In this work a first $\varphi_{1s}^{\mathrm{I}}$ was first calculated with $V = -2/r_>$. Then $\varphi_{1s}^{\mathrm{II}}$ was calculated from V of Eq. (2) with $\varphi_{1s}^{\mathrm{I}}$ used in Eq. (2). Since $\varphi_{1s}^{\mathrm{II}}$ is less tightly bound than a self-consistent solution of the Schrödinger equation using $V(r)$, this effects a partial compensation for neglect of $k \geqslant 2$ terms of Eq. (1) in $V(r)$. All the approximations made at this stage are corrected by calculating the higher order terms in the perturbation expansion.

It was found that the single-particle energy ϵ_{1s} is $-0.578\,48$ a.u.; so $E^{(0)}$ equals $-1.15696+(1.4)^{-1}$ a.u. The first-order energy correction $E^{(1)}$ is given by $\langle 1s\,1s|v|1s\,1s\rangle - 2\langle 1s\,1s\,\mathrm{II}|v|1s\,1s\,\mathrm{II}\rangle$ and equals $-0.593\,28$. Then $E^{(0)}+E^{(1)}$ equals $-1.035\,95$ a.u. as compared with the very accurate value $-1.174\,474\,6$ a.u. of Kołos and Wolniewicz.[5]

We have used perturbation theory to calculate the second-order energy corrections. The second order diagrams are shown in Fig. 1, and these terms were evaluated as in previous atomic calculations.[3] The infinite number of bound excit-

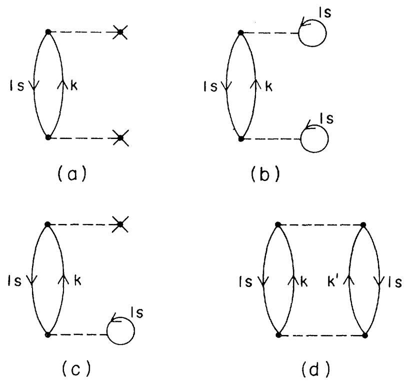

FIG. 1. Second-order energy diagrams. The crossed interaction equals the interaction of Eq. (1) minus V of Eq. (2).

ed states were included by the n^{-1} rule, and sums over continuum states were evaluated by numerical integration.[3] The second-order results are listed in Table I. The contribution from the correlation diagram of Fig. 1(d) is −0.047 26 a.u., and our result for the total energy through second order is −1.165 72 a.u. Figure 1(d) with $l \geqslant 2$ accounts for the corrections due to lack of spherical symmetry.

The third-order diagrams which are expected to contribute most are shown in Fig. 2. Diagram 2(c) also occurs inverted. Values for these diagrams are given in Table I. When these third-order contributions are added to the second-order result, we obtain −1.176 16 a.u. as compared with the accurate value[5] of −1.174 474 6 a.u.

In analogy to the atomic case,[3] we expect the third-order and higher order correlation energy diagrams to be small (approximately 0.002 a.u.) since our excited states in this case are calculated in the field of $N-1$ other electrons, where $N = 2$ for H_2. We also note that small contributions will come from higher l values which were not included in our second- and third-order results. The methods of this paper should be very useful in calculating the energy of larger molecules, just as they have been successfully applied to many-electron atoms.[3] For many molecules the initial approximation of a spherically symmetric potential is better than it is for H_2.

We have also used our single-particle states to calculate the static dipole polarizability of H_2. The polarizability

$$\alpha_{\parallel} = -2E^{(2)}, \qquad (3)$$

where $E^{(2)}$ is the second-order shift in energy due to the perturbation z. Similarly, $\alpha_{\perp}$ is given by Eq. (3) with $E^{(2)}$ now the second-order energy due to two interactions with x. The energy $E^{(2)}$ includes all terms with two interactions with z (or with x for $\alpha_{\perp}$) and any number of interactions with

$$\sum_{i=1}^{N}\left[-\sum_{k}\frac{2r_<^{\,k}}{r_>^{\,k+1}}P_k\cos(\theta_i)-V(r_i)\right]+\sum_{i<j} r_{ij}^{-1}, \qquad (4)$$

where $N = 2$ for H_2.

In lowest order, $\alpha_{\parallel}$ and $\alpha_{\perp}$ equal 1.035 Å^3. In the next order we include one interaction with the terms of Eq. (4), and $\alpha_{\parallel}$ and $\alpha_{\perp}$ are now 1.095 and 0.628 Å^3, respectively. A rough calculation of higher order terms gives the result 0.972 Å^3 for $\alpha_{\parallel}$ and 0.689 Å^3 for $\alpha_{\perp}$, which is in

Table I. Energy contributions in a. u.

Diagram	Energy in a.u.
Second-Order (Fig. 1).[a]	
(a) k(ℓ = 2)	-.07495
(a) k(ℓ = 4)	-.00597
(a) k(ℓ = 6)	-.00131
(b) + (c)	-.00028
(d) ℓ = 0	-.00918
(d) ℓ = 1	-.03258
(d) ℓ = 2	-.00431
(d) ℓ = 3	-.00119
Subtotal	-.12977
Third-Order (Fig. 2).	
(a) k(ℓ = 2), k'(ℓ = 2)	-.00908
(a) k(ℓ = 2), k'(ℓ = 4)	-.00197
(a) k(ℓ = 4), k'(ℓ = 2)	-.00197
(a) k(ℓ = 4), k'(ℓ = 4)	-.00030
(b) + (c) k(ℓ = 2), k'(ℓ = 2)	+.00288[b]
Subtotal	-.01044

[a] l values refer to the excited states.

[b] Inverted diagram of Fig. 2(c) included.

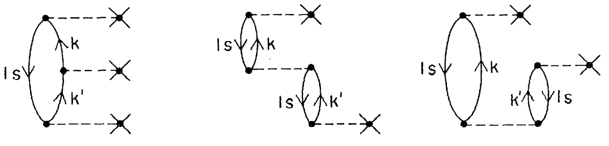

FIG. 2. Third-order energy diagrams involving two or three crossed interactions. The crossed interaction is given by Eq. (1) minus $V(r)$ of Eq. (2). Diagram 2(c) also occurs inverted.

reasonable agreement with the accurate calculation of Kołos and Wolniewicz.[6] Our results for $\alpha_{\|}$ and $\alpha_{\perp}$ are probably accurate to 5%.

Upon completion of this work, I became aware that expansions about a single molecular center have been used previously in variational calculations. Extensive reviews have been given by Bishop[7] and by Hayes and Parr.[8]

I wish to acknowledge helpful discussions with J. Bloor, G. B. Hess, J. Schulman, and R. L. Somorjai.

---

*Work supported by the Aerospace Research Laboratories, Office of Aerospace Research, U. S. Air Force, Contract No. F33615-69-C-1048.

[1] K. A. Brueckner, Phys. Rev. 97, 1353 (1955).
[2] J. Goldstone, Proc. Roy. Soc. (London), Ser. A 239, 267 (1957).
[3] H. P. Kelly, Phys. Rev. 131, 684 (1963), and 136 B896 (1964), and 144, 39 (1966).
[4] J. C. Slater, Quantum Theory of Molecules and Solids (McGraw-Hill Book Company, Inc., New York, 1963), Vol. I.
[5] W. Kołos and L. Wolniewicz, J. Chem. Phys. 41, 3663 (1964).
[6] W. Kołos and L. Wolniewicz, J. Chem. Phys. 46, 1426 (1967).
[7] D. M. Bishop, in Advances in Quantum Chemistry, edited by P. O. Löwdin (Academic Press, Inc., New York, 1967), Vol. III, p. 25.
[8] E. F. Hayes and R. G. Parr, Progr. Theoret. Phys. (Kyoto) Suppl. 40, 78 (1967).

TWO-FREQUENCY HYPERFINE TRANSITIONS IN ATOMIC DEUTERIUM*

J. D. McCullen,† W. S. Smith, and W. J. Tipton
Department of Physics, University of Arizona, Tucson, Arizona 85721
(Received 14 July 1969)

A modified fast-passage transition scheme, using two frequencies, is described and discussed.

The Abragam-Winter adiabatic fast-passage technique[1] for causing transitions between atomic hyperfine states has been widely employed in preparing atom beams for use in polarized ion sources and hydrogen masers. This paper reports a variation on this technique, using Happer's[2] two-frequency transition scheme, which proves useful for deuterium beams. It permits two possible populations of the deuterium hyperfine states with much the same weak-field transition system as is appropriate for hydrogen.

The atomic beam considered in both these and the adiabatic fast-passage experiments is a hydrogen or deuterium beam which has been initially state selected by passage through an inhomogenous focusing magnetic field. The beam consists of atoms in the set of hyperfine levels for which dE/dH is positive at high magnetic field H. (See Fig. 1.) In the fast-passage method these atoms are passed through a weak gradient magnetic field which provides a region of "static," but slowly increasing, magnetic field in which there is also an rf field. The rf frequency is chosen to be the atomic transition frequency at some median value of the "static" magnetic field. With sufficient rf field strength present, the atom will maintain a precession about the rf field (in a reference frame rotating at the rf frequency) while the "static" field slowly sweeps through resonance, and hyperfine transitions will result.

Following Happer,[2] we can write the Hamiltonian for the atom in the combined "static" and fast-passage rf fields as

$$\mathcal{H}=\mathcal{H}_f+g_J\mu_0J_zH_c+g_J\mu_0H_{\mathrm{rf}}(J_x\cos\omega_1t+J_y\sin\omega_1t). \tag{1}$$

$\mathcal{H}_f$ is the free-atom term, and the next two terms represent the interaction of the electron magnetic moment with the external magnetic fields H_c and H_{rf} (nuclear terms are neglected). If Eq. (1) is transformed to a coordinate system rotating about the z direction with frequency ω_0, the form is changed to

$$\mathcal{H}'=\mathcal{H}_f+g_J\mu_0J_zH_c-\omega_0F_z+g_J\mu_0H_{\mathrm{rf}}[J_x\cos(\omega_1-\omega_0)t+J_y\sin(\omega_1-\omega_0)t]. \tag{2}$$

F_z here is the total atomic spin projection (including nuclear spin), while J_x, J_y, and J_z as in Eq. (1) are electron spin projections. It is clear that if $\omega_1=\omega_0$, this Hamiltonian admits of stationary solutions, since $\mathcal{H}'$ in that case is time independent. The energies of these eigenstates will in general depend on ω_1 and H_{rf}. When H_{rf} is zero, the energies W_i resulting from Eq. (2) are readily calculated;