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Many-Body Perturbation Calculation of the Indirect Spin-Spin Coupling Constant in HD Molecule*

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The linked-cluster many-body perturbation approach has been applied to the study of indirect nuclear spin-spin coupling constant J_{HD} in HD molecule. The complete set of states used were the bound and continuum states of H_2^+ molecular ion with the internuclear separation appropriate to H_2 molecule. Our calculated value of J_{HD} through the Fermi contact interaction mechanism is +42.57 Hz in good agreement with the most recent experimental value of +42.7 ± 0.7 Hz.

Although the indirect spin-spin interaction between nuclei in molecules has been utilized extensively for qualitative understanding of electronic structures in molecules, its quantitative calculation even for the simple molecule HD has proved to be a formidable task, with the current situation far from conclusive.[1-8] The various theoretical approaches utilized so far can be divided broadly into two categories. In the first category is the conventional second-order perturbation as first proposed by Ramsey and Purcell.[1,2] The difficulty with such an approach is that one requires a knowledge of the complete set of ground and excited states of the molecule, which is not usually available.[3]

To obviate the knowledge of excited states, variation-perturbation procedures have been used by a number of authors.[4-8] In one class of such calculations, a diagonal-type perturbation procedure[4,5] was used, the second-order energy due to the hyperfine field of one nucleus being minimized to obtain the first-order perturbed wave function of the molecule. This function was then utilized to calculate the cross term in the second-order energy involving the other nucleus to obtain J_{HD}. The difficulty with this procedure was that the second-order nuclear self-coupling energy is infinite in nonrelativistic theory, no real minimum thus being attainable in a variational approach. A second class of variation perturbation calculation has attempted to extremize the cross terms in the second-order energy proportional to J_{HD} using variational functions which describe the first-order perturbation due to both nuclei.[6-9] The difficulty with this procedure is that the cross term due to two perturbations has by itself no minimum and one does in fact get oscillatory behavior as the number of parameters increased.[9]

In this paper, we have revived the perturbation approach in a form that meets the major difficulty, namely, a knowledge of a complete set of states for the molecule. This is accomplished by using the linked-cluster many-body perturbation theory (LCMBPT),[10] where a neighboring Hamiltonian $\mathcal{H}_0$, for which the complete set of states can be obtained exactly, is used as the starting point for a perturbation treatment of $\Delta\mathcal{H} = \mathcal{H} - \mathcal{H}_0$. In our work here, a multiple perturbation approach is used in conjunction with the LCMBPT, using the sum of $\Delta\mathcal{H}$ and the two hyperfine interaction Hamiltonians $\mathcal{H}_H'$ and $\mathcal{H}_D'$ associated with the two nuclei. For the speed of convergence of the perturbation approach, it is necessary that the basis states chosen (and hence $\mathcal{H}_0$) describe the behavior of the charge densities near the nuclei reasonably well. In particular, a one-center choice for $\mathcal{H}_0$ might be expected to be rather inadequate for the present problem since this would require the inclusion of very high angular-momentum states to describe properly the charge densities near the nuclei. With this consideration in view, the H_2^+ molecular-ion Hamiltonian was chosen for $\mathcal{H}_0$. This has the dual merit of providing a basis set that is both exactly derivable and has the desirable cusp behavior at the nuclei.

The procedure of calculation follows broadly the same lines as that employed in handling atomic systems subject to external perturbations.[11] Only a very brief description will be presented here with emphasis on some of the points that have special importance for the present problem. The starting Hamiltonian, corresponding to two noninteracting electrons in the H_2^+ molecule framework, is given (in atomic units) by

$$\mathcal{H}_0=\sum_{i=1}^{2}\left(-\tfrac{1}{2}\nabla_i^2-\frac{1}{r_{\mathrm{H}i}}\frac{1}{r_{\mathrm{D}i}}\right), \tag{1}$$

leading to $\Delta\mathcal{H}=1/r_{12}$. The net perturbation Hamiltonian $\mathcal{H}'$ composed of $\Delta\mathcal{H}$ and the hyperfine interaction terms is then given by

$$\mathcal{H}'=(1/r_{12})+\mathcal{H}_{\mathrm{H}}'+\mathcal{H}_{\mathrm{D}}', \tag{2}$$

where the $\mathcal{H}_A'$ ($A=\mathrm{H}$ or D) are given by

$$\mathcal{H}_A'=\frac{16\pi}{3}\frac{\mu_{\mathrm{B}}\mu_A}{e^2a_0^2}\sum_{i=1}^{2}\vec{\mathrm{I}}_A\cdot\vec{\mathrm{S}}_i\delta(\vec{\mathrm{r}}_{Ai}), \tag{3}$$

μ_{B} and μ_A representing the Bohr magneton and nuclear magnetic moment of nucleus A and $\vec{\mathrm{I}}_A$ and $\vec{\mathrm{S}}_i$ the nuclear and electron spin operators. Following the usual linked-cluster perturbation approach, the total energy correction ΔE is given by

$$\Delta E=\sum_{n,n'}\langle\Phi_0|u_n(\infty,0)\mathcal{H}_I'(0)u_{n'}(0,\infty)|\Phi_0\rangle_L, \tag{4}$$

the suffix L and other quantities in Eq. (4) having their usual meanings in linked-cluster perturbation theory.[11] The indirect nuclear spin-spin interaction Hamiltonian has the form

$$\mathcal{H}_{\mathrm{HD}}=hJ_{\mathrm{HD}}\vec{\mathrm{I}}_{\mathrm{H}}\cdot\vec{\mathrm{I}}_{\mathrm{D}}. \tag{5}$$

The spin-spin coupling constant J_{HD} can be evaluated by equating the expectation values of both sides of Eq. (5) over the nuclear spin states with magnetic quantum numbers $M_{\mathrm{H}}=I_{\mathrm{H}}$ and $M_{\mathrm{D}}=I_{\mathrm{D}}$. The expectation value ΔE_{HD} of the left-hand side of Eq. (5) corresponds to the energy derived from Eq. (4), keeping one order in $\mathcal{H}_{\mathrm{H}}'$ and one order in $\mathcal{H}_{\mathrm{D}}'$ and all possible orders in $1/r_{12}$. In diagrammatic representation, the corresponding diagrams must contain the $\mathcal{H}_{\mathrm{H}}'$ and $\mathcal{H}_{\mathrm{D}}'$ vertices once, whereas the $1/r_{12}$ vertex can occur any number of times. Since the spin Hamiltonian is isotropic, it is sufficient to work with only the z-component term in Eq. (5).

For the one-electron basis set for the diagrammatic evaluation of ΔE_{HD} we have utilized the exact bound and continuum states of $\mathcal{H}_0$ which correspond to H_2^+ molecular-ion wave functions for the internuclear distance $R=1.4$ a.u. These are expressed in the form

$$\rho_i(\lambda,\mu,\varphi)=\Lambda_i(\lambda)M_i(\mu)e^{im\varphi}, \tag{6}$$

where $\Lambda_i(\lambda)$ and $M_i(\mu)$ are functions of the elliptic coordinates, $\lambda_j=(r_{j\mathrm{H}}+r_{j\mathrm{D}})/R$, $\mu_j=(r_{j\mathrm{H}}-r_{j\mathrm{D}})/R$, and $r_{j\mathrm{H}}$ and $r_{j\mathrm{D}}$ are the distances of the jth electron from H and D nuclei. For the bound states, we have to determine both the energy eigenvalues as well as the eigenfunctions described by Eq. (6).[12] This requires the solution of the appropriate second-order differential equations for $\Lambda_i(\lambda)$ and $M_i(\mu)$ which are coupled by the energy and a separation constant A_i. The eigenvalues and eigenfunctions for some of the lower bound states are already available in the literature.[12] For the higher bound states, only eigenvalues are available[13] and we had to solve the necessary continued-fraction equations to obtain A_i and $M_i(\mu)$. The functions $\Lambda_i(\lambda)$ were obtained by solving the corresponding differential equation numerically.[14] For the continuum states, the eigenvalues are, of course, $\epsilon_i=k^2/2$. Again A_i and $M_i(\mu)$ are obtained by solving the requisite continued-fraction equations and $\Lambda_i(\lambda)$ through numerical integration of the corresponding differential equation.[14]

The diagrams involved in the calculation of ΔE_{HD} are similar in form to those one encounters in the perturbation of atomic systems in an external field.[11] The external fields in the present molecule are the hyperfine fields of nuclei at the sites of the electrons. For the hyperfine operators $\mathcal{H}_{\mathrm{H}}'$ and $\mathcal{H}_{\mathrm{D}}'$ we have utilized wiggly lines terminating with dots in the diagrams. The lowest-order diagram for the present calculation is of second order involving one order each in $\mathcal{H}_{\mathrm{H}}'$ and $\mathcal{H}_{\mathrm{D}}'$. The higher orders involve additional vertices associated with $1/r_{12}$. Figure 1 shows the second-order and all of the third-order diagrams. The typical fourth-order diagrams involving two hyperfine vertices and two $1/r_{12}$ ver-

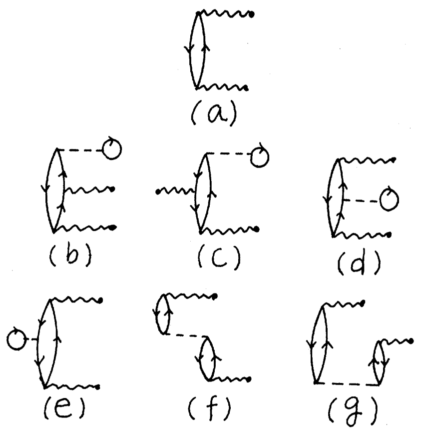

FIG. 1. Second- and third-order diagrams for the spin-spin interaction in HD molecule. The wiggly line denotes the Fermi contact operators $\mathcal{H}_H'$ and $\mathcal{H}_D'$.

tices are shown in Fig. 2. We have included all the distinct diagrams that are obtained from those in Fig. 2 by taking account of time reordering and permutations of the vertices among themselves and between hole and particle lines. The most time-consuming aspect of the evaluation of diagrams was the calculation of matrix elements associated with the vertices. The hyperfine vertices only require the density of the wave functions at the nuclei and are straightforward. However, the matrix elements of $1/r_{12}$, particularly those involving continuum states, require special attention, since elliptic coordinates are involved. We have utilized the procedure developed by Rüdenberg[15] for variational molecular bound-state calculations. Our computer program for this purpose was checked by comparing our values for a few two-center two-electron integrals using Slater orbitals with currently available tables for such integrals.[16] It should be pointed out that because of the use of elliptic coordinates, the integration over the continuum states involves a somewhat different multiplying factor than in atomic work,[17]

$$\sum_k \to (2/\pi R)^2 \int_0^\infty dk.$$

The second-order diagram (1a) represents the contribution to J_{HD} from two noninteracting electrons in the ground state of a H_2^+ molecular ion with internuclear separation of $R = 1.4$ a.u. The third-order diagrams (1b)-(1g) represent the contribution to J_{HD} from the first-order effect of $1/r_{12}$ on diagram (1a). Of these, diagrams (1b)-(1e) represent the role of the passive Hartree-Fock interaction between the electrons which converts the electronic wave functions from those of H_2^+ molecular ion to the H_2 molecule. Diagrams (1f) and (1g) represent the influence of two-particle self-consistency effects in the perturbed state of the system when the nuclear hyperfine interaction is switched on.

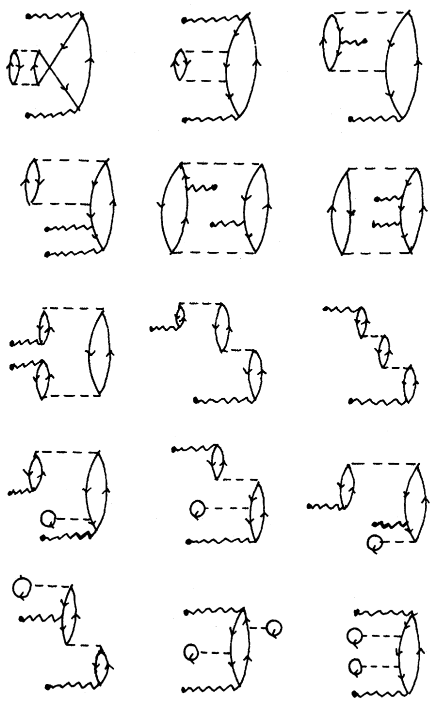

FIG. 2. Some typical fourth-order diagrams for the spin-spin interaction in HD molecule.

The contributions to J_{HD} from various diagrams are listed in Table I. For the second-order diagram (1a) we have separately listed the contributions from gerade and ungerade particle states. A rather substantial cancelation is seen to occur between the two types of excitations in this order. For the diagrams (1b)-(1g), the contributions are listed after the gerade and ungerade cancelations have been carried out, wherever they occur. For the sake of brevity, only the net contribution from all the fourth-order diagrams is listed. The third-order result is seen to be about one-half of the second order. This somewhat slow decrease up to this order is a result of the rather severe cancelation between gerade and ungerade excitations in second order. However, on comparing individual diagrams, even the diagram with the largest contribution in third order is found to be a factor of 4 smaller than the smaller (gerade) of the second-order diagrams. This situation is reminiscent of the hyperfine interaction problems in atomic oxygen,[18] nitrogen, and phosphorus,[19] where the low-

Table I. Contributions from various diagrams to J_{HD}.

Order of perturbation		Diagrams	Contributions (Hz)
Second order		(1a) gerade	−385.65
		(1a) ungerade	458.67
	Subtotal		73.02
Third order		(1b)	−74.76
		(1c)	−10.16
		(1d)	−47.60
		(1e)	47.41
		(1f)	24.90
		(1g)	24.90
	Subtotal		−35.31
Fourth order	Subtotal		4.86
	Grand total		42.57
	Experiment		42.7 ± 0.7

est order core-polarization diagrams have rather substantial cancelations which make the higher orders of crucial importance.

In fourth order, there is strong cancelation among the various diagrams due to the gerade and ungerade symmetry and spins. Additionally, there is also substantial cancelation among different types of diagrams leading to the net relatively small contribution shown in Table I, namely, about 6.7% of the second-order result. We have carried out rough estimation of important fifth-order diagrams and find that this strong cancelation persists and that the net contribution in this order is expected to be no more than a cycle. Our result compares very favorably with the experimental value of +42.7 ± 0.7 Hz.[20] The experimental value does include small contributions from second-order effects involving dipolar and orbital hyperfine interactions. Several estimates[3,4] of these contributions have been made in the literature which are consistently rather small. It is our feeling[21] that these mechanisms do not contribute more than the quoted range of experimental error. We would like to point out that the present procedure can also be used to evaluate these additional contributions to J_{HD}.

It is worth mentioning that in contrast to LCMBPT calculations on atomic systems, laddering procedures to sum over selected classes of diagrams are not suitable in the present approach. This is because the diagrams (1d) and (1e) which are the progenies of the usual hole-hole and hole-particle ladders are comparable in importance with the other diagrams in third order and it is not appropriate to selectively apply laddering procedure to any one class of diagrams. Instead, the correct procedure for the present problem is to sum all diagrams for each order and such a sum is seen from our work to show satisfactory convergence. It should be pointed out that in earlier work, Matcha and Brown[22] and Goodisman[23] had used a zero-order H_2^+ basis set, as in the present work, and utilized variation-perturbation procedures to calculate the energies of the ground and excited states of H_2 molecule with rather satisfactory results. The convergence observed here using the same starting Hamiltonian for a complex property such as the spin-spin coupling constant demonstrates the general validity of the ionic basis set as a starting point for perturbation calculations on diatomic molecules.

It has been possible to carry out this calculation of the indirect spin-spin coupling constant due first to the increased sophistication attained in recent years in applying LCMBPT procedures to atomic systems and secondly to the advance in computing techniques which makes it practicable to work with one-electron continuum states of molecular systems. It is expected that the present procedure would be easily applicable to other hyperfine and magnetic properties of hydrogen molecule involving double perturbation by external sources, such as the rotational moment and spin-rotation constant.

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Formation and Structure of Electrostatic Collisionless Shocks*

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A one-dimensional, two-species numerical-simulation code has been used to study the formation and structure of collisionless electrostatic shocks formed by two colliding plasmas and by a plasma striking a perfectly reflecting piston. Collisionless shocks are formed in hydrogen up to a maximum piston velocity of $M \equiv v_D/c_S \sim 3.5$. Shocks with velocities up to $M \sim 4$ have been produced which have a predominantly laminar structure accompanied by strong collisionless dissipation.

Theoretical models for electrostatic shocks in the absence of a magnetic field have been discussed by a number of authors.[1-5] Low-Mach-number $[M=v_D/c_S<2$, where $c_S=(T_e/m_i)^{1/2}]$ shocks have been experimentally produced by Alikhanov, Belon, and Sagdeev[6] and Taylor, Baker, and Ikezi,[7] and numerically simulated by Mason[5] and Sakanaka, Chu, and Marshall.[8] In this Letter we discuss formation of stable, high-Mach-number electrostatic shocks by means of the particle-in-cell simulation technique[9] treating both the ions and electrons exactly with the mass ratio of hydrogen (1836). Since the electrons are treated exactly instead of isothermally, the critical Mach number of $M \sim 1.6$ does not apply. The shocks described here are well approximated by a rapid change from one equilibrium state to another with little or no fluctuations in the shock front (although perhaps having large fluctuations behind the front), and thus correspond most closely to the "laminar"[1-4] rather than "turbulent"[5] model.

Initial conditions.—The shocks discussed here are created in two ways. The first method consists of a plasma of ions and electrons moving to the right with Mach number M, as shown in Fig. 1(a), with the plasma initially $(T=0)$ just in contact with the right-hand, perfectly reflecting wall. The plasma is sustained at the left by continually injecting a Maxwellian plasma. The second method is similar but with the above plasma filling only the left half of the box and an equal-density plasma with Mach number of opposite sign occupying the right half. This configuration clearly should generate two shocks which differ only statistically. For $M<1$ a shock will readily form on the basis of the ion-ion instability[10] in one dimension. Shocks formed with $M>1$ do so by means of the nonlinear process described below.

Theory of formation and structure.—In the two initial conditions used, the method of shock for-