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MANY-BODY THEORY FOR HYPERFINE EFFECTS IN ATOMS AND MOLECULES (*)

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Résumé. — Comme exemple d'application de la théorie des perturbations à *N*-corps, nous avons étudié le problème de la constante J_{HD} de couplage spin-spin nucléaire indirect dans la molécule HD. L'ensemble complet d'états utilisé est exactement celui des états des spectres discret et continu de l'ion moléculaire H_2^+, avec la même séparation internucléaire que pour la molécule H_2. Notre valeur calculée de J_{HD} par le mécanisme d'interaction de contact de Fermi est 42,57 Hz, alors que la plus récente valeur expérimentale est de 42,7 ± 0,7 Hz.

Abstract. — Results of application of linked-cluster many-body pertubations theory to atomic hyperfine constants are reviewed and as a specific example of the application of this procedure to molecular systems, we have studied the problem of the indirect nuclear spin-spin coupling constant J_{HD} in HD molecule. The complete set of states used were the exact bound and continuum states of H_2^+ molecular ion, with the same internuclear separation as for the H_2 molecule. Our calculated value of J_{HD} through the Fermi contact interaction mechanism is + 42.57 Hz as compared to the most recent experimental value of + 42.7 ± 0.7 Hz.

1. **Introduction.** — The linked-cluster many-body perturbation theory (LCMBPT) approach, also referred to in the literature as the Brueckner-Goldstone procedure [1, 2] has been demonstrated in recent years to be greatly successful in handling the influence of many-body effects on atomic properties. Our experience [3, 4] with this procedure leads us to single out four particularly attractive features of this procedure in the treatment of atomic properties :

(1) It eliminates the element of choice that is crucial for variational procedures. Thus, in handling a system described by a Hamiltonian $\mathcal{H}$, once a neighboring Hamiltonian $\mathcal{H}_0$ is chosen for which one can determine a complete set of states, the perturbation Hamiltonian is definite, namely $\Delta\mathcal{H} = \mathcal{H} - \mathcal{H}_0$. One is then assured that if a perturbation procedure is carried out involving all orders in $\Delta\mathcal{H}$ one must end up with the correct energy and wave functions for the system.

(2) The analysis of perturbation terms through the use of diagrammatic techniques permits insight into the physical meaning of various terms. With some practice, one then develops some intuition about those diagrams that are most important for the order of accuracy desired. This is of great help when the total number of contributing diagrams is rather large.

(3) The third feature which we find very advantageous is the fact that one utilizes perturbation theory, dealing with small numbers, rather than the difference of large ones. This is particularly important when dealing with small energies related, for example, to polarizabilities and hyperfine constants. In the latter case, the core-polarization contribution from an inner shell in the LCMBPT approach is calculated directly instead of as the difference of large numbers as in the Unrestricted Hartree-Fock procedure.

(4) The fourth attractive feature of the LCMBPT procedure is that once one has a basis set for a certain choice of $\mathcal{H}_0$, the same set may be used not only for studying correlation energies and other properties of the isolated atom including many-body effects, but also to study properties of the atom in the presence of external fields.

The success of the LCMBPT procedure in the treatment of hyperfine effects in isolated atoms can be seen from Table I and Table II. Table I presents the experimental results for the isotropic hyperfine constants a (in the hyperfine spin-Hamiltonian a **I**.**J**) in a number of atoms, together with the predictions of restricted Hartree-Fock theory. The difference between the experimental and restricted Hartree-Fock constants are referred to as the experimental correlation contributions to a. In Table II, we list the values of a that we have calculated using LCMBPT theory employing a starting Hamiltonian involving what is known in the literature [1, 2] as a V^{N-1} potential. As an additional point of comparison, the theoretical and experimental correlation contributions are listed next to each other in the last two columns. The most remarkable example is the case of phosphorus where RHF

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TABLE I

Table of experimental values and expected correlation contributions for atomic hyperfine constants

Atom and nucleus	R. H. F. value a (MHz)	Expt. value a (MHz)	Expt. correlation contribution Δa (MHz)
$^3He(^3S_1)$	4 479.23 ([a])	4 493.134 2 ([c])	13.90
$^7Li(^2S_{1/2})$	285.01 ([b])	401.756 ([f])	116.75
$^7Li(^2P_{3/2})$	− 6.470 2 ([b])	− 3.073 ([g])	− 3.397
$^{11}B(^2P_{3/2})$	70.685 8 ([c])	73.347 ([h])	2.661
$^{14}N(^4S_{3/2})$	0	10.45 ([i])	10.45
$^{23}Na(^2S_{1/2})$	622.644 ([d])	885.813 1 ([f])	262.8
$^{31}P(^4S_{3/2})$	0	55.055 691 ([j])	55.055 691

([a]) SKLAREW (R. C.) and CALLAWAY (J.), *Phys. Lett.* (Netherlands), 1967, **25A**, 177.
([b]) GOODINGS (D. A.), *Phys. Rev.*, 1961, **123**, 1706.
([c]) Value obtained from clementis analytic wave-functions (Supp. to IBM. *J. Res. and dev.*, 1965, **9**, 2) using 2.688 5 nuclea magnetons for the magnetic moment of ^{11}B.
([d]) LEE (T.), DUTTA (N. C.) and DAS (T. P.), *Phys. Rev.*, 1970, **1A**, 995.
([e]) ROSNER (S. D.) and PIPKIN (F. M.), *Phys. Rev.*, 1970, **A 1**, 571.
([f]) KUSCH (P.) and TAUB (H.), *Phys. Rev.*, 1949, **75**, 1477.
([g]) BROG (K. C.), ECK (T. G.) and WIDER (H.), *Phys. Rev.*, 1967, **153**, 91.
([h]) WESSEL (G.), *Phys. Rev.*, 1953, **92**, 1581.
([i]) ANDERSON (L. W.), PIPKIN (F. M.) and BAIRD (J. C.), *Jr. Phys. Rev.*, 1959, **116**, 87.
([j]) LAMBERT (R. H.) and PIPKIN (F. M.), *Phys. Rev.*, 1962, **128**, 198.

TABLE II

Comparison of many-body theoretical and experimental atomic hyperfine constants

Atom	Theoretical value (MHz)	Experimental value (MHz)	Correlation theory	Correlation expt.
$^3He(^3S_1)$	4 491.87 ([a])	4 493.134 2	12.64	13.90
$^7Li(^2S_{1/2})$	399.05 ([b])	401.756	114.04	116.75
$^7Li(^2P_{3/2})$	− 2.790 6 ([c])	− 3.073	3.679 6	3.397
$^{14}N(^4S_{3/2})$	10.488 ([d])	10.45	10.488	10.45
$^{23}Na(^2S_{1/2})$	872.8 ([e])	885.813 1	249.8	262.81
$^{31}P(^4S_{3/2})$	49.80 ([f])	55.055 691	49.80	55.055 691
$^{11}B(^2P_{3/2})$	73.91 ([g])	73.347	3.21	2.661

([a]) DUTTA (N. C.), MATSUBARA (C.), PU (R. T.) and DAS (T. P.), *Bull. A. Phys. Soc.*, 1968, **13**, 392.
([b]) CHANG (E. S.), PU (R. T.) and DAS (T. P.), *Phys. Rev.*, 1968, **174**, 1.
([c]) LYONS (J. D.), PU (R. T.) and DAS (T. P.), *Phys. Rev.*, 1969, **178**, 103.
([d]) DUTTA (N. C.), MATSUBARA (C.), PU (R. T.) and DAS (T. P.), *Phys. Rev.*, 1969, **177**, 33.
([e]) LEE (T.), DUTTA (N. C.) and DAS (T. P.), *Phys. Rev.*, 1970, **A 1**, 995.
([f]) DUTTA (N. C.), MATSUBARA (C.), PU (R. T.) and DAS (T. P.), *Phys. Rev. Letters*, 1968, **21**, 1139.
([g]) RODGERS (J. E.), DUTTA (C. M.) and DAS (T. P.), *Bull. Am. Phys. Soc.*, 1970, **15**, 1521.

theory leads to $a = 0$ and UHF theory [5] as well as one-electron exchange core polarization diagrams from LCMBPT calculations lead to a wrong sign compared to experiment. It is only after the contributions from the correlation diagrams in the LCMBPT procedure are included that one gets agreement in sign and fairly close agreement in magnitude with experiment.

In addition to the atoms listed, a number of others have also been studied. Oxygen atom in the ground ^3P state has been studied by Kelly [6]. In this case, as well as in the excited state (^2P) of lithium atom [7] and ground state (^2P) of boron atom studied in our group, since the atoms do not have spherical symmetry, one gets in addition to the contact term, a contribution to the total magnetic hyperfine constant from the classical electron-nuclear dipolar and nuclear electron orbit interactions and also the nuclear quadrupole interaction term. Additionally, among the transition metal atoms, the isotropic hyperfine constant in iron atom (Fe^{57}) in its ground state has been studied by Kelly (reported at this Conference) and we are studying neutral manganese atom and Mn^{++} ion.

The overall conclusions from Tables I and II and the other systems that have been studied recently is that the evaluation of diagrams involving two orders in $\Delta\mathcal{H} = \mathcal{H} - \mathcal{H}_0$, and certain ladder dia-

grams which can be summed to all orders, is sufficient to excellent answers for the hyperfine constants of isolated atoms.

This success of the LCMBPT procedure for isolated atom properties has prompted us to apply it to more complicated problems of hyperfine effects in interacting atoms and in molecules. In the work [8] on hyperfine effects of interacting atoms, we have been concerned with the problem of the hyperfine constant of hydrogen atom interacting with helium and neon atoms at long range. This analysis is important for the understanding of hyperfine pressure shifts of hydrogen atom in atmospheres of rare gases [9, 10]. As a by-product of these calculations, we have obtained [8] the van der Waals energy of hydrogen, helium, and neon atoms interacting among themselves and with one another. In the field of hyperfine effects of molecules, we have studied the problem of the indirect spin-spin interaction constant between proton and deuteron in HD molecule. This interaction is of great importance from a chemical point of view because of the insight it provides into the electronic structure of molecules, yet it is not quantitatively understood in the relatively simple system, HD molecule, through the use of conventional perturbation or variational procedures [11]. Due to limitations of time, we shall not be able to discuss the first topic, namely the hyperfine interaction of interacting atoms, but refer the readers to our published work in this field. The second topic, namely the problem of spin-spin interaction in HD molecule will be the main theme of our talk.

II. Spin-spin interaction in HD molecule. — The indirect spin-spin interaction between nuclei A and B is described by the spin-Hamiltonian,

$$\mathcal{H}_S = J\mathbf{I}_A.\mathbf{I}_B\,.$$

For HD molecule, the experimental alue of J is known to be $+ 42.7 \pm 0.7$ Hz. The explanation of the origin of J was first given by Ramsey and Purcell [13] who showed that the spin-Hamiltonian $\mathcal{H}_S$ resulted from the second-order hyperfine energy of the molecule composed of one order each in the hyperfine Hamiltonian for the two nuclei. They used conventional perturbation theory in their work which involves the energies and wave-functions of the excited states of the molecule including continuum states. Unfortunately, such information is never available except for a few of the low lying excited states and so one cannot use this procedure for quantitative analysis. In our work, using the LCMBPT procedure [1, 2], we have revived the perturbation approach in a form that meets this major difficulty of conventional perturbation theory. What is done is to use a zero order Hamiltonian $\mathcal{H}_0$ which is close to the actual Hamiltonian $\mathcal{H}$ for the molecule, but for which the complete set of eigenstates can be obtained exactly in contrast to the situation for $\mathcal{H}$. The procedure for calculating J is then one of handling a perturbation problem involving three perturbation Hamiltonians, namely $\Delta\mathcal{H} = \mathcal{H} - \mathcal{H}_0$ and the hyperfine Hamiltonians of the two nuclei.

For 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 [14] 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 properly describe 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 [4, 8]. The starting Hamiltonian, corresponding to two non-interacting electrons in the H_2^+ molecular framework is given by : (in atomic units)

$$\mathcal{H}_0 = \sum_{i=1}^{2}\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_{Hi}} - \frac{1}{r_{Di}}\right) \tag{1}$$

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

$$\mathcal{H}' = \frac{1}{r_{12}} + \mathcal{H}'_H + \mathcal{H}'_D \tag{2}$$

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

$$\mathcal{H}'_A = \frac{16\pi}{3}\,\frac{\mu_B\,\mu_A}{e^2}\,a_0^2 \sum_{i=1}^{2} \mathbf{I}_A.\mathbf{S}_i\,\delta(r_{Ai}) \tag{3}$$

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

$$\Delta E = \sum_{n,n'} < \Phi_0 \mid U_n(\infty, 0)\,\mathcal{H}'_i(0)\,U'_n(0, -\infty) \mid \Phi_0 >_L \tag{4}$$

the suffix L and other quantities in eq. (4) having their usual meanings in linked-cluster perturbation theory [3, 4, 8]. The indirect nuclear spin-spin interaction Hamiltonian has the form :

$$\mathcal{H}_{HD} = hJ_{HD}\,\mathbf{I}_H.\mathbf{I}_D\,. \tag{5}$$

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 $M_H = I_H$ and $M_D = I_D$. 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 $\mathcal{H}'_H$ and one order in $\mathcal{H}'_D$ and all possible orders in $1/r_{12}$. In diagrammatic representation, the corresponding diagrams must contain the $\mathcal{H}'_H$ and $\mathcal{H}'_D$ 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 the H_2^+ molecular ion wave functions for internuclear distance $R = 1.4$ a. u. These are expressed in the form

$$\Phi_i(\lambda, \mu, \varphi) = \Lambda_i(\lambda)\, M(\mu)\, e^{im\varphi} \qquad (6)$$

where $\Lambda_i(\lambda)$ and $M_i(\mu)$ are functions of the elliptic coordinates, $\lambda = (r_{iH} + r_{iD})/R$, $\mu = (r_{iH} - r_{iD})/R$ and r_{iH} and r_{iD} are the distances of the ith 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) [15]. 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 [15]. For the higher bound states, only eigenvalues are available [16] 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 [17]. For the continuum states, the eigenvalues are, of course, $\varepsilon_i = k^2/2$. Again Λ_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 [17].

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 [4]. The external fields in the present molecule are the hyperfine fields of nuclei at the sites of the electron. For the hyperfine operators $\mathcal{H}'_H$ and $\mathcal{H}'_D$ we have utilized in the diagrams wiggly lines terminating with dots. The lowest order diagram for the present calculation is of second order involving one order each in $\mathcal{H}'_H$ and $\mathcal{H}'_D$. The higher orders involve additional vertices associated with $1/r_{12}$. In referring to the order of the diagrams in the rest of the paper we shall only count the number of $1/r_{12}$ vertices. Figure 1 shows the zero order and all of the first order diagrams. Figure 2 gives the important second order diagrams.

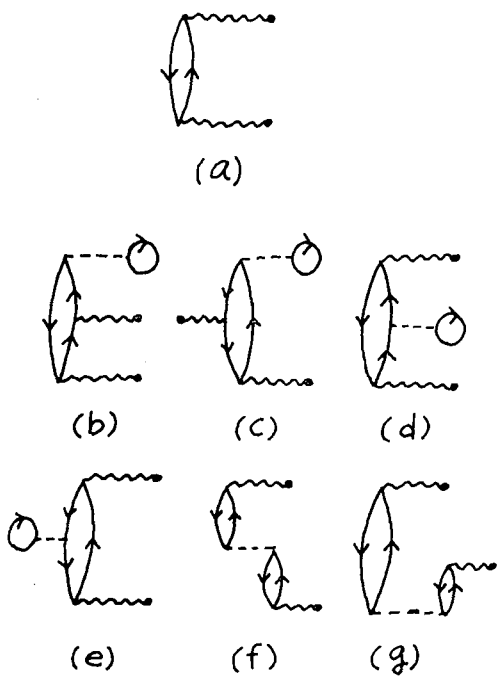

FIG. 1.

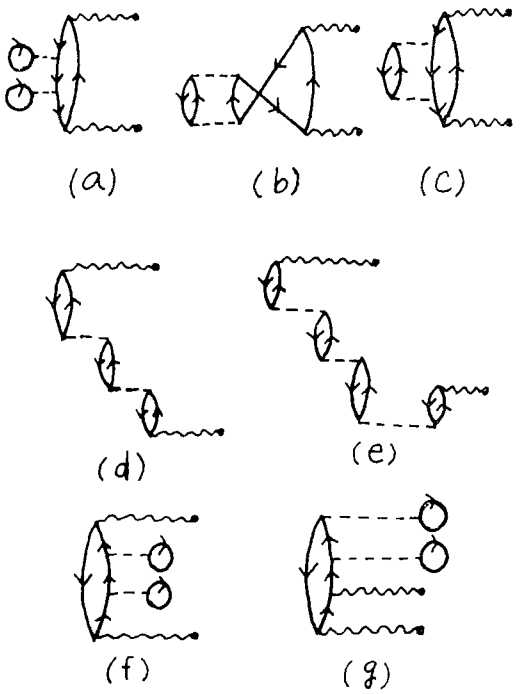

FIG. 2.

The most time consuming aspect of the evaluation of diagrams was the calculation of matrix element associated with the vertices. The hyperfine vertices require only the density of the wave-functions at the nuclei and are straightforward. However, the matrix elements of $-/r_{12}$, particularly those involving continuum states, require special attention, since elliptic coordinates are involved. We have utilized the procedure developed by Rüdenberg [18] for variational molecular bound state calculations. Our computer program was checked by comparing the results obtained with available tables for molecular bound state two-electron integrals. The integration in k over the continuum states also involves a somewhat different multiplying factor than in atomic work [20] because of the use of elliptic coordinates, namely

$$\sum_k \to \left(\frac{2}{\pi R}\right)^2 \int_0^\infty dk\,.$$

The second order diagram (1*a*) represents the contribution to J_{HD} from two non-interacting electrons in the ground state of H_2^+ molecular ion with the internuclear separation of $R = 1.4$ a. u. The third order dia-

grams (1*b*)-(1*g*) can be divided, for purposes of nomenclature and physical understanding of their origin, into three classes. Class I is described by diagrams (1*b*) and (1*c*), class II by diagrams (1*d*) and (1*e*) and class III by diagrams (1*f*) and (1*g*). The first two classes represent the influence of the passive interaction between electrons which converts the electronic wavefunctions from those of the H_2^+ molecular ion to the H_2 molecule. The only reason we make a distinction between these classes is that in the literature on the LCMBPT approach to atomic problems the class II diagrams have usually been associated with hole-hole and hole-particle ladders. The class III diagrams represent the influence of self consistency effects on the perturbed states produced by the nuclear moments. In figures (2*a*)-(2*j*), we have given the representative fourth order diagrams. A number of these diagrams ((2*a*)-(2*f*)) can be generated by combinations of the classes of diagrams described under third order, while the others ((2*g*)-(2*j*)) can not be obtained in this way and occur for the first time in fourth order. Thus, diagrams (2*a*) originate from a combination of class I with itself. Diagram (2*b*) arises from a combination of classes I and II, diagrams (2*c*) from class II with itself, diagrams (2*d*) from combination of classes I and III, diagrams (2*e*) from combination of classes II and III and diagrams (2*f*) from class III with itself. Diagrams (2*g*) to (2*j*) are those which originate for the first time in fourth order. This list completes all classes of diagrams that can appear in fourth order.

The contribution to J_{HD} from all these various diagrams are listed in Table III. The major contribution arises from the second order diagram (1*a*) with severe cancellation from the gerade and ungerade particle states. In evaluating this diagram as well as all the rest, bound excited states $ns\sigma_g$ for $n = 2 - 5$, $np\sigma_u$ for $n = 2 - 6$, $nd\sigma_g$ for $n = 3 - 6$, $nf\ \sigma_u$ for $n = 4$ and 5 (n and l referring to the united atom designation) were utilized. The continuum states include l values ranging from 0 to 11. As a result of substantial cancellations between gerade and ungerade excited states, the convergence in l was slow for the continuum contributions and we had to go up to $l = 11$. The bound excited states were found to contribute about 34 % of the contribution from diagram (1*a*), while the rest of the contribution came from the continuum states. This result indicates that in any variational or other types of calculation of spin-spin interaction constants, care must be taken to include the influence of continuum states either directly or indirectly.

For the third order diagrams, we have listed the combined contribution from gerade and ungerade particle excitations. It should be mentioned here that, in contrast to the second order case, the bound state contribution in both third and fourth orders represent larger percentages of the total contribution. The reason for this is the presence of the low lying $2p\sigma_u$ state which can appear more than once as excited state, correspondingly increasing the contribution of the diagrams concerned through the accompanying small energy denominators. The net third order contribution is seen to cancel out almost one half of the second order contribution. The fourth order contribution is much smaller but significant. It can be noticed from Table III that the contributions of all the classes of diagrams in the third and fourth orders are in general comparable. Consequently, there is no particular class of diagrams that justifies inclusion to all orders through the familiar laddering process. In particular, diagrams (1*d*) and (1*e*) are the usual progenies of the hole-particle, hole-hole ladders of atomic problems, where one starts from the Hartree-Fock V^{N-1} approximation. In the present situation, these two diagrams are seen to make nearly equal and opposite contributions and it is not justified to carry out the hole-hole and hole-particle laddering separately. Physically, this near cancellation of (1*d*) and (1*e*) corresponds to the comparable influence of the passive interaction between electrons on the energies of hole and particle

TABLE III

Contributions from various diagrams to J_{HD}

Order of perturbation	Diagrams	Contributions
Second order	(1 a) gerade	− 385.65
	(1 a) ungerade	458.67
	Subtotal	73.02
Third order [a]	(1 b)	− 74.76
	(1 c)	− 10.16
	(1 d)	− 47.60
	(1 e)	47.41
	(1 f)	24.90
	(1 g)	24.90
	Subtotal	− 35.31
Fourth order [a,b]	(2 a)	12.54
	(2 b)	11.33
	(2 c)	− 1.20
	(2 d)	− 42.08
	(2 e)	4.60
	(2 f)	48.38
	(2 g)	− 1.20
	(2 h)	2.70
	(2 i)	3.02
	(2 j)	− 33.23
	Subtotal	4.86
	Grand total	42.57
	Experiment	42.7 ± 0.7

[a] All possible combinations of the gerade and ungerade excited states were included.

[b] All the entries listed under the fourth order diagrams refer not only to the diagrams shown in Fig. 2, but also all other diagrams of similar topologies obtained by various possible time orderings of interaction vertices and interchange of the latter between hole and particle lines.

states, leaving their difference nearly the same. The net result we obtained for the contact contribution to J_{HD} is 42.57 $\pm$ 2 Hz. The confidence limit quoted is actually rather conservative. We have made rough estimates of the contributions from the typical diagrams of fifth order which originate from various classes of the fourth order diagrams and found their contribution well within the assumed limit. The additional flexibility in the confidence limit was introduced to take account of certain approximations made in the évaluation of the diagrams, namely neglect of the contributions from $l > 11$, from non-σ particle states in the fourth order diagrams, and particle-particle triple and quadruple continuum excitation matrix elements. The inclusion of the effects of these factors would have required an excessive amount of computer time. Our final result compares quite favorably with the experimental value of + 42.7 $\pm$ 0.7 Hz [12]. The experimental value of course includes small additional contributions from the dipole-dipole and orbital interactions [21]. These latter effects can also be evaluated by the same LCMBPT procedure that we have used here for the contact contribution.

III. **Conclusion.** — We have presented an example of the practical application of the LCMBPT approach to systems more complicated than isolated atoms. The procedure used here is expected to be equally successful for other properties of H_2 molecule, particularly those properties which depend crucially on the neighborhood of the nucleus such as the electric field-gradient at the deuteron and the spin-rotation constant. Another method that we are presently exploring involves a one-center united atom model [22]. This has been found to be quite successful for the correlation energy and electric field at the fluorine nucleus of HF molecule and its success for hyperfine properties is being tested currently.

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