Electron-Nuclear Coupling in the Hyperfine Structure of the Hydrogen Molecular Ion

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A perturbation theory for determining the electron-nuclear coupling corrections to the adiabatic expectation values of operators of molecular systems is developed and applied to the hyperfine Hamiltonian of the hydrogen molecular ion. The expectation values of the Fermi contact parameter for the rotation-vibration states $N=1$, $v=4$-8 are compared with experimental results. Previous adiabatic expectation values differ from the empirical values by about 600 kHz. Inclusion of the first-order corrections reduces the discrepancies to less than 9 kHz.

Calculations of the properties of molecules are usually carried out within a single-channel approximation in which the molecular eigenfunction is written as a product of an electronic wave function and a nuclear wave function and the action of the nuclear kinetic-energy operator on the electronic wave function is ignored. In the Born-Oppenheimer approximation, the nuclei are assumed to move in the field generated by averaging over the electronic wave function. In the standard adiabatic approximation, the field is modified by the addition of the diagonal expectation values of the nuclear and electronic kinetic-energy operators.[1-3]

Elaborate calculations of the Fermi contact parameter for H_2^+ have been carried out within the standard adiabatic approximation and compared to the empirical values derived by Jefferts[4] from his measurements on the hyperfine transitions in the $N=1$ rotational levels of the $v=4$-8 vibrational levels.[5,6] The values are of the order of 800 MHz and the discrepancies between theory and experiment are about 600 kHz.

We show that the standard adiabatic approximation for the nuclear motion should be modified. We also introduce a perturbation theory for electron-nuclear corrections in a molecular system and carry out precise calculations of the first-order contribution to the contact parameter. The discrepancies are reduced to less than 9 kHz.

The Schrödinger equation for H_2^+ is, in atomic units,

$$[-\nabla^2/2 - \nabla^2/8m^* - \nabla_R^2/2m^*$$
$$+ V_{el}(r,R) + V_{nu}(R) - E]\Psi(r,R) = 0, \quad (1)$$

where r is the position vector of the electron measured with respect to the midpoint of the nuclei, R is the vector joining the nuclei, $m^* = \frac{1}{2} M_p$ with M_p the proton mass,

$$V_{el}(r,R) = -1/|r - \tfrac{1}{2}R| - 1/|r + \tfrac{1}{2}R|, \quad (2)$$

$$V_{nu}(R) = 1/R, \quad (3)$$

and E is the eigenvalue.[2]

Expand the molecular wave function $\Psi(r,R)$ as a sum of products of electronic eigenfunctions $\phi_j(r;R)$ and nuclear eigenfunctions $\chi_{j\gamma}(R)$,

$$\Psi(r,R) = \sum_{j\gamma} \phi_j(r;R)\chi_{j\gamma}(R), \quad (4)$$

where j and γ represent, respectively, the electronic and nuclear quantum numbers.

In the Born-Oppenheimer approximation, the wave functions $\phi_j(r;R)$ with R fixed in space depend parametrically on R and are solutions of the Schrödinger equation

$$H_{el}\phi_j(r;R) = V_j(R)\phi_j(r;R), \quad (5)$$

where H_{el} is the electronic Hamiltonian at the separation R given by

$$H_{el} = -\tfrac{1}{2}\nabla^2 + V_{el}(r,R). \quad (6)$$

Then substituting the expansion Eq. (4) into Eq. (1), we obtain

$$\left\{\frac{-1}{2m^*}\nabla_R^2 + V_j(R) + V_{nu}(R) - E\right\}\chi_{j'\beta}(R) + \frac{1}{2m^*}\sum_{j\gamma}\{2i\mathbf{B}_{j'j}\cdot\nabla_R + C_{j'j}\}\chi_{j\gamma}(R) = 0, \quad (7)$$

where

$$C_{j'j} = -\langle\phi_{j'}|\nabla_R^2 + \tfrac{1}{4}\nabla^2|\phi_j\rangle, \quad \mathbf{B}_{j'j} = i\langle\phi_{j'}|\nabla_R|\phi_j\rangle. \quad (8)$$

The Born-Oppenheimer approximation is obtained by ignoring the off-diagonal matrix elements and $C_{j'j'}$ and $\mathbf{B}_{j'j'}$. The standard adiabatic approximation retains the terms involving the diagonal expectation values of ∇_R^2 and ∇^2.

A slightly improved adiabatic approximation is obtained by requiring that the electronic eigenfunctions be solutions of Schrödinger's equation with the electronic Hamiltonian[7]

$$\tilde{H}_{el} = -\tfrac{1}{2}\nabla^2[1 + 1/4m^*] + V_{el}(r,R), \quad (9)$$

which we shall call the scaled electronic Hamiltonian. Then a similar process yields the set of coupled equations[8]

$$\left\{ \frac{-1}{2m^*}\nabla_R^2 + \tilde{V}_{j'}(R) + V_{\mathrm{nu}}(R) - E \right\}\tilde{\chi}_{j'\beta}(R) + \frac{1}{2m^*}\sum_{j\gamma}\{2i\tilde{\mathbf{B}}_{j'j}\cdot\mathbf{V}_R + \tilde{C}_{j'j}\}\tilde{\chi}_{j\gamma}(R) = 0 , \tag{10}$$

where

$$\tilde{C}_{j'j} = -\langle\tilde{\phi}_{j'}|\nabla_R^2|\tilde{\phi}_j\rangle, \quad \tilde{\mathbf{B}}_{j'j} = i\langle\tilde{\phi}_{j'}|\mathbf{V}_R|\tilde{\phi}_j\rangle , \tag{11}$$

and in which the off-diagonal matrix elements are ignored to obtain the improved adiabatic approximation.

For the state represented by the wave function $\Psi^{(0)}(\mathbf{r},\mathbf{R})$, the Fermi contact parameter is given by[9]

$$b_{1F} = c_F(\langle\Psi^{(0)}(\mathbf{r},\mathbf{R})|\delta(\mathbf{r}_a)|\Psi^{(0)}(\mathbf{r},\mathbf{R})\rangle) , \tag{12}$$

where the outer parentheses represent integration over R, and

$$c_F = \tfrac{8}{3}\pi g_e g_N \mu_0 \mu_N , \tag{13}$$

and g_e and g_N are the electron and proton g factors, respectively, μ_0 and μ_N are the Bohr and nuclear magnetons, respectively, and $\mathbf{r}_a$ is the position vector of the electron measured from one of the nuclei. Let

$$\Psi^{(0)}(\mathbf{r},\mathbf{R}) = \tilde{\phi}_0(\mathbf{r};R)\tilde{\chi}_{0\beta}(\mathbf{R}) , \tag{14}$$

with $\tilde{\phi}_0$ the $1s\sigma_g$ ground electronic state obtained from the scaled electronic Hamiltonian of Eq. (9). Then in the improved adiabatic approximation,

$$\tilde{b}_{1F}(R) = c_F\langle\tilde{\phi}_0|\delta(\mathbf{r}_a)|\tilde{\phi}_0\rangle \tag{15}$$

and the value for the contact parameter is given by

$$b_{1F} = (\tilde{\chi}_{0\beta}|\tilde{b}_{1F}(R)|\tilde{\chi}_{0\beta}) . \tag{16}$$

We have determined $\tilde{\phi}_0(\mathbf{r};R)$ and $\tilde{V}_0(R)$ by solving Eq. (9) by the variational method using the basis set of σ_g symmetry

$$F_k(\lambda,\mu,R) = 2\lambda^{l_k}\mu^{m_k}\exp(-\alpha\lambda)\cosh(\beta\mu) , \tag{17}$$

where l_k is an integer, m_k is an even integer, $k = 1, \ldots, P$ with P the number of basis functions, and λ and μ are prolate spheroidal coordinates for the electron measured from the nuclei. The parameters α and β were varied at each R to minimize the $1s\sigma_g$ energy $\tilde{V}_0(R)$. The improved adiabatic nuclear wave functions $\tilde{\chi}_{0\beta}(\mathbf{R})$ used in determining b_{1F} were obtained by the numerical integration of the equation

$$\{(1/2m^*)[-\nabla_R^2 + \tilde{C}_{00}] + \tilde{V}_0(R) + V_{\mathrm{nu}}(R)\}\tilde{\chi}_{0\beta}(\mathbf{R})$$
$$= E_{0\beta}\tilde{\chi}_{0\beta}(\mathbf{R}) . \tag{18}$$

A check on the accuracy was provided by the scaling relation

$$\tilde{b}_{1F}(R) = \kappa b_{1F}(\rho R) , \tag{19}$$

$b_{1F}(R)$ being obtained from the eigenfunction ϕ_0 of the

Hamiltonian of Eq. (6),

$$b_{1F}(\overline{R}) = \kappa c_F\langle\phi_0|\delta(\mathbf{r}_a)|\phi_0\rangle , \tag{20}$$

where[8,9] $\overline{R} = \rho R$, $\kappa = \rho^3$, $\rho = (1 + 1/4m^*)^{-1}$. At the equilibrium internuclear distance $R = 2.0$ the values of $b_{1F}(R)$ agree to better than 1 kHz with those reported by McEachran, Veenstra, and by Cohen[6] and Carrington and Kennedy.[10]

The adiabatic values of b_{1F} are listed in Table I. We multiplied the values given by McEachran, Veenstra, and Cohen by 0.999 974 96 to correspond to modern values of the physical constants.[12] The difference between the two sets of values arises, we believe, because although McEachran, Veenstra, and Cohen scaled their results for $b_{1F}(\overline{R})$ obtained using Eq. (20) by the factor κ, they did not scale $\overline{R}$ by ρ^{-1} prior to averaging over $\chi_{0\beta}$.

Table I also contains the empirical values inferred by Jefferts[4] for the $N = 1$ rotational level of the vibrational levels $v = 4$–8. There occurs a discrepancy of about 600 kHz for each rotation-vibration level.

The discrepancies may arise from the inadequacy of

TABLE I. For the rotational level $N = 1$ of the vibrational levels $v = 4$–8 calculations and experimental determinations of the Fermi contact parameter b_{1F} and the electron-nuclear coupling correction Δb_{1F} in MHz. Numbers in parentheses represent the quoted experimental error in the last digit.

v	Adiabatic Ref. 6[b]	Adiabatic This work	Expt.[a] Ref. 4[c]	Correction This work	Total This work
4	837.1792	837.3402	836.743(2)	−0.5887	836.752
5	819.6896	819.8362	819.239(2)	−0.5890	819.247
6	803.6509	803.7827	803.186(2)	−0.5897	803.193
7	789.9975	789.1151	788.519(2)	−0.5907	788.524
8	775.6768	775.7786	775.182(2)	−0.5919	775.187

[a]Another fit to the experimental data of Jefferts was carried out by Kalaghan in an unpublished thesis (Ref. 11) with results that are 16 kHz lower for $v = 4$ and 10 kHz lower for $v = 8$. It is not clear whether the data were the same as those analyzed by Jefferts (Ref. 4) so this fit has not been included in the table. The thesis was an early attempt to resolve the discrepancy between theory and experiment by including the first-order electron-nuclear coupling contribution but because of insufficient accuracy the numerical results were not persuasive.
[b]Multiplied by the factor 0.999 974 96 to correspond to modern values of the physical constants.
[c]The theoretical relation $b_{1F} = b + \tfrac{1}{3}c$ was used with the experimentally inferred b and c.

the adiabatic approximation in representing the electronic wave functions. The first-order correction to the electronic wave function $\tilde{\phi}_0$ appearing in $\Psi^{(0)}(\mathbf{r},\mathbf{R})$ in Eq. (14) may be written as

$$\tilde{\phi}_0^{(1)}(\mathbf{r};R) = \frac{-1}{2m^*}\sum_{j\neq0}\left[\frac{|\tilde{\phi}_j\rangle[\langle\tilde{\phi}_j|\nabla_R^2|\tilde{\phi}_0\rangle + 2\langle\tilde{\phi}_j|\nabla_R|\tilde{\phi}_0\rangle\cdot\nabla_R]}{\tilde{V}_0(R) - \tilde{V}_j(R)}\right] = f_0^{(1)}(\mathbf{r};R) + 2\mathbf{g}_0^{(1)}(\mathbf{r};R)\cdot\nabla_R , \tag{21}$$

where the summation includes an integration over the continuum states. The first-order correction is

$$\Delta b_{1F} = 2c_F(\tilde{\chi}_{0\beta},\langle\tilde{\phi}_0|\delta(\mathbf{r}_a)|\tilde{\phi}_0^{(1)}\rangle\tilde{\chi}_{0\beta}) . \tag{22}$$

To evaluate Eq. (22), we need to consider only states of σ_g symmetry and we may choose the electronic and nuclear wave functions to be real. The wave function $\tilde{\phi}_0^{(1)}$ may be determined variationally by minimizing the functionals

$$J = \langle f_0^{(1)}|\tilde{H}_{\text{el}} - \tilde{V}_0(R)|f_0^{(1)}\rangle + 2\langle f_0^{(1)}|\nabla_R^2|\tilde{\phi}_0\rangle \tag{23}$$

and

$$K = \langle g_{0;r}^{(1)}|\tilde{H}_{\text{el}} - \tilde{V}_0(R)|g_{0;r}^{(1)}\rangle + 2\langle g_{0;r}^{(1)}|\frac{\partial}{\partial R}|\tilde{\phi}_0\rangle , \tag{24}$$

with the $P\ \tilde{\phi}_j$ obtained from the diagonalization of the Hamiltonian Eq. (9) using the set Eq. (17), with the operators expressed in prolate spheroidal coordinates. For K only the radial spheroidal polar component $g_{0;r}^{(1)}$ of $\mathbf{g}_0^{(1)}$ relative to the nuclear midpoint is required due to the σ_g symmetry.[8] The number of basis functions P was increased until convergence to four figures was reached.

The first-order corrections were averaged over the improved adiabatic nuclear wave functions $\tilde{\chi}_{0\beta}$ with the results listed in Table I. They reduce the discrepancy with the experimental values from 600 to at most 9 kHz.

Thus electron-nuclear coupling effects on the distribution of electron charge explain most of the difference between theory and experiment. We are extending the perturbation theory in an attempt to identify the sources of the remaining discrepancy.

Perturbation theory offers several advantages over other methods of including electron-nuclear couplings in molecular systems such as the direct variational approach[1,13] which is limited to low-lying vibrational states and cannot be readily applied to off-diagonal matrix elements.

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