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THE NUCLEAR-QUADRUPOLE-INDUCED DIPOLE MOMENT OF HD

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We calculate in a simple MO way the dipole moment induced in HD by the nuclear quadrupole of the deuteron, as a function of the internuclear separation. We find a reversal of the direction of the dipole with increasing internuclear separation, for which we note indirect experimental evidence. As a check on the accuracy of our result we also calculate the electric field gradient induced at the D nucleus by an external electric field, per unit external field, which for exact theory would be exactly the same function. The form of the function so obtained is indeed similar – although not identical – to that for the dipole moment. The dipole moment at the equilibrium internuclear separation is ≈ 0.075 atomic units per unit quadrupole moment, directed $H^- \rightarrow D^+$. (For the measured quadrupole moment of the deuteron, this is $\approx 2 \times 10^{-11}$ D.) However, we find the induced field gradient at the deuteron for this separation to be 0.094 atomic units per unit external field, in the *opposite* direction.

1. Introduction

The ground state of the deuteron in HD has nuclear spin $I=1$, so the electric potential of which it is the source can and does have a quadrupolar component. The potential felt by the two electrons in the molecule is thus not symmetric under exchange of the two nuclei, and we expect a corresponding asymmetry in the distribution of electron density. The lowest-order moment of the asymmetry is a slight dipole moment, which, because of the cylindrical symmetry of the molecule, is directed along the internuclear axis. We have calculated this nuclear-quadrupole-induced dipole moment, using a simple molecular orbital (MO) approach, to first order in the strength of the quadrupole.

Formally the induced dipole moment is given, by ordinary second-order perturbation theory, as

$$\langle \mu(Q_0) \rangle = 2 \sum_{N \neq 0} \frac{\langle 0 | \mu | N \rangle \langle N | Q_D | 0 \rangle}{E^{(0)} - E^{(N)}}. \quad (1)$$

The states $|N\rangle$ are the electronic states of H_2 within the Born–Oppenheimer approximation, and the energies $E^{(N)}$ are the corresponding energies. ($|0\rangle$ is the ground state and $E^{(0)}$ the ground state energy.) Because of the cylindrical symmetry of the molecule, the only non-zero component of the dipole moment will be that along the internuclear axis. Therefore μ is the operator for the component of the dipole moment along the internuclear axis. Q_D is the electric potential produced by the quadrupole of magnitude Q_0 located at the deuteron, and R is the internuclear separation. (Note that the breakdown of the BO approximation in HD gives rise to a well-known [1–6] dipole moment in HD, approximately 10^5 times larger than that which we calculate to be induced by the nuclear quadrupole. First predicted by Wick [1], the rotational–vibrational spectrum due to

this larger moment was first observed by Herzberg [2]. Note that the quadrupole-induced dipole would persist even were the nuclei in fact of infinite mass.

2. MO calculation of the induced dipole

We first calculate the ground-state wavefunctions of the *separate* deuterium and hydrogen atoms in the presence of the quadrupole to first order in the magnitude of the quadrupole. This we do using ordinary time-independent perturbation theory, in a manner similar to the calculation of long-distance forces by Dalgarno and Lewis [7]. The resulting atomic orbitals (AOs) we label $\psi_{\text{H}}^0(r_{\text{H}})$, $\psi_{\text{H}}^1(r_{\text{H}}, \mathbf{R}, Q_0)$, $\psi_{\text{D}}^0(r_{\text{D}})$, $\psi_{\text{D}}^1(r_{\text{D}}, Q_0)$, where ψ_{H}^0 and ψ_{D}^0 are the unperturbed ground-state wavefunctions of the hydrogen and deuterium atoms, and ψ_{H}^1 and ψ_{D}^1 are the first-order corrections to them, r_{H} is the distance of the electron from the proton, r_{D} the distance from the deuteron, \mathbf{R} the internuclear separation, and Q_0 the magnitude of the quadrupole.

We now construct the physical space part of our molecular orbital (MO) out of the simplest possible linear combination of the AOs:

$$\Psi(\mathbf{r}, \mathbf{R}, Q_0) = [2(1+S_0)]^{-1/2} [\psi_{\text{H}}^0 + \psi_{\text{D}}^0 + \psi_{\text{H}}^1(Q_0) + \psi_{\text{D}}^1(Q_0)] \quad (2)$$

where S_0 is the usual H_2 overlap integral:

$$S_0 = \int d^3r \psi_{\text{H}}^0 \psi_{\text{D}}^0 = e^{-R} (1 + R + \frac{1}{3}R^2) \quad (3)$$

Note that this wavefunction is normalized correctly only to zeroth order in Q_0 . This serves in this case because the expectation value of the dipole moment operator is zero to zeroth order in Q_0 . Thus the *unnormalized* quantity $\langle \Psi | \mu | \Psi \rangle$ contains no terms less than first order in Q_0 , and the normalization factor we divide it by need contain no terms higher than zeroth order in Q_0 .

Our complete MO is then

$$\Psi_{\text{MO}}(\mathbf{r}_1, \mathbf{r}_2, \sigma_1, \sigma_2, \mathbf{R}, Q_0) = \Psi(\mathbf{r}_1, \mathbf{R}, Q_0) \Psi(\mathbf{r}_2, \mathbf{R}, Q_0) \chi(\sigma_1, \sigma_2) \quad (4)$$

where \mathbf{r}_1, σ_1 are the space and spin coordinates of the first electron and \mathbf{r}_2, σ_2 those of the second. χ is the usual singlet (antisymmetric) spin eigenstate.

The symmetry of the molecule and quadrupole assures us that the dipole moment will lie along the internuclear axis. So we let that be the z axis of our coordinate system, and use for the magnitude of dipole moment operator (in atomic units):

$$\mu = (\frac{1}{2}R - z_1) + (\frac{1}{2}R - z_2) \quad (5)$$

The z_1 and z_2 refer to the z coordinates of the two electrons. Note that we are measuring the moment from midway between the two nuclei. This simplifies the calculation. We locate the proton at the origin and the deuteron on the positive z axis at distance R .

Using eqs. (5), (4) and (2) the expectation value of the dipole moment operator, keeping no terms higher than first order in Q_0 , is

$$\begin{aligned} &\langle \mu(R, Q_0) \rangle \\ &= \frac{2}{1+S_0} \int d^3r [\psi_{\text{H}}^0(\frac{1}{2}R - z) \psi_{\text{H}}^1(Q_0) + \psi_{\text{H}}^0(\frac{1}{2}R - z) \psi_{\text{D}}^1(Q_0) + \psi_{\text{D}}^0(\frac{1}{2}R - z) \psi_{\text{H}}^1(Q_0) + \psi_{\text{D}}^0(\frac{1}{2}R - z) \psi_{\text{D}}^1(Q_0)] \end{aligned} \quad (6)$$

where we have summed over spin, dropped the superfluous subscripts on the z 's, and used the normalization of the physical space component of the MO given in eq. (2) above. The leading factor of 2 in eq. (6) is due

to the presence of two electrons. Let the four integrals in eq. (6) be denoted, in order, μ_I , μ_{II} , μ_{III} , and μ_{IV} .

Because of the cylindrical symmetry of the molecule, only the part of the quadrupole proportional to Y_2^0 will couple to the dipole moment operator. So our perturbation is given explicitly by

$$Q_D = Q_0 \frac{1}{c_{20}} Y_2^0(\theta_D) \frac{1}{r_D^3}, \quad (7)$$

where $c_{20} = \frac{1}{4}(5/\pi)^{1/2}$ is the numerical factor in Y_2^0 . Ordinary first-order perturbation theory then gives the following differential equation that $\psi_D^1(Q_0)$ must satisfy:

$$(H_D^0 - E_D^0) \psi_D^1(Q_0) = (E_D^1 - Q_D) \psi_D^0, \quad (8)$$

where H_D^0 is the Hamiltonian for the electron in a deuterium atom and E_D^0 is the corresponding ground-state energy. E_D^1 is the first-order energy shift, which is clearly zero. We try the solution

$$\psi_D^1(r_D, Q_0) = f(r_D) Q_0 \frac{1}{c_{20}} Y_2^0(\theta_D) \psi_D^0 \quad (9)$$

and upon substituting this and the right-hand side of eq. (7) into eq. (8) obtain the following differential equation for $f(r_D)$:

$$\left[-\frac{1}{2} \frac{d^2}{dr_D^2} + \left(1 - \frac{1}{r_D}\right) \frac{d}{dr_D} + \frac{3}{r_D^2} \right] f(r_D) = -\frac{1}{r_D^3}. \quad (10)$$

A particular solution of this suited to our needs is

$$f(r_D) = -\left(\frac{1}{3r_D} + \frac{1}{9}\right). \quad (11)$$

Thus

$$\psi_D^1(r_D, Q_0) = -Q_0 \frac{1}{c_{20}} Y_2^0(\theta_D) \left(\frac{1}{3r_D} + \frac{1}{9}\right) \psi_D^0(r_D). \quad (12)$$

Note that this is orthogonal to the ground state. By this and the orthogonality of the Y_l^m (in particular Y_2^0 to Y_1^0), we see immediately that

$$\mu_{IV} = 0. \quad (13)$$

Using eq. (12) we calculate μ_{II} ; it is

$$\mu_{II} = -4Q_0 \{ \text{Ei}(2R) (\cosh R D_1 - \sinh R D_2) - e^{-R} [i \text{Ei}(2R) (D_1 + D_2) + D_3] \}, \quad (14)$$

where D_1 , D_2 , and D_3 are the following polynomials in R :

$$D_1(R) = \frac{2R}{3} + \frac{50}{R} + \frac{420}{R^3}, \quad D_2(R) = 8 + \frac{190}{R^2} + \frac{420}{R^4}, \quad D_3(R) = \frac{25R}{9} + \frac{80}{3} + \frac{440}{3R} + \frac{420}{R^2} + \frac{840}{R^3}. \quad (15)$$

The two non-elementary functions, similar to the usual exponential-integral function, are defined as follows:

$$\text{Ei}(u) = \int_u^\infty dt \frac{e^{-t}}{t}, \quad i \text{Ei}(u) = \int_0^u dt \frac{1 - e^{-t}}{t}. \quad (16)$$

We use the same approach to calculate μ_I . The formal representation of $\psi_H^1(Q_0)$ is

$$|\psi_H^1(Q_0)\rangle = \sum_{n \neq 0} \frac{|\psi_H^{0(n)}\rangle \langle \psi_H^{0(n)} | Q_D | \psi_H^{0(0)} \rangle}{E^{(n)} - E^{(0)}}. \quad (17)$$

Therefore

$$\mu_1 = \sum_{n \neq 0} \frac{\langle \psi_H^{0(0)} | \frac{1}{2}R - z | \psi_H^{0(n)} \rangle \langle \psi_H^{0(n)} | Q_D | \psi_H^{0(0)} \rangle}{E^{(n)} - E^{(0)}} \quad (18)$$

or, going back to wavefunctions:

$$\mu_1 = \int d^3r \psi_H^1(\mu_0) Q_D \psi_H^0, \quad (19)$$

where $\psi_H^1(\mu_0)$ is the first-order correction to ψ_H^0 due to a perturbation $\mu_0(\frac{1}{2}R - z)$. We put in for the strength of the perturbation μ_0 - here equal exactly to 1 - to emphasize the complementarity of ψ_H^1 to ψ_D^1 . Using the same method as before, we solve for $\psi_H^1(\mu_0)$, obtaining

$$\psi_H^1(r_H, \mu_0) = -\mu_0 \frac{1}{c_{10}} Y_1^0(\theta_H) \left(\frac{1}{2}r_H^2 + r_H \right) \psi_H^0(r_H), \quad (20)$$

where $c_{10} = \frac{1}{2}(3/\pi)^{1/2}$ is the numerical factor in Y_1^0 . Using this, we calculate μ_1 , and get

$$\mu_1 = -Q_0 \left[\frac{27}{2R^4} - e^{-2R} \left(2R^2 + 6R + 9 + \frac{18}{R} + \frac{27}{R^3} + \frac{27}{2R^4} \right) \right]. \quad (21)$$

This leaves μ_{III} , for which we must find $\psi_H^1(Q_0)$. Again we use the same approach, but this time there is no obvious form to try for the solution to the first-order differential equation

$$(H_H^0 - E_H^0) \psi_H^1(Q_0) = (E_H^1 - Q_D) \psi_H^0. \quad (22)$$

However, we note that Q_D can fortuitously be written as

$$Q_D = Q_0 \frac{1}{c_{20}} \frac{\partial^2}{\partial R^2} \frac{1}{|r_H - R|}. \quad (23)$$

Substituting this for Q_D in eq. (22), we then expand both it and $\psi_H^1(Q_0)$ in Y_l^m , using the usual expansion of $1/|r_H - R|$. We exchange the order of summation and all other operators. Equating coefficients of the Y_l^m on both sides of the equation then produces second-order differential equations in r_H for the coefficients in the expansion of $\psi_H^1(Q_0)$. These we solve using truncated power series. (A log term is needed for the Y_0^0 term). It then turns out that we can contract the expansion of $\psi_H^1(Q_0)$ to

$$\psi_H^1(Q_0) = \psi_H^0(r_H) \left[\left(r_H + \ln r_H - \frac{1}{2r_H} \right) E_H^1(R, Q_0) - Q_0 \int dr_H \left(1 + \frac{1}{r_H} \right) \frac{1}{|r_H - R|} \right]. \quad (24)$$

Note that the integral is indefinite, thus ambiguous. The best form of the integral for our purposes is

$$\int dr_H \left(1 + \frac{1}{r_H} \right) \frac{1}{|r_H - R|} = -\frac{(r_H + 1)z_D}{Rr_D^3} + \frac{r_H + 2}{R^2r_D} - \frac{1}{R^2} - \frac{2}{R^3} \ln \left(\frac{r_D - z_D}{r_H - z_H} \right). \quad (25)$$

Using the right-hand side of eq. (25) in the right-hand side of eq. (24) makes the latter solve eq. (22).

$\psi_H^1(Q_0)$ is not a well-behaved function. It has a strong infinity at the location of the deuteron, a logarithmic singularity between the two nuclei along the internuclear axis, and a pole of order one at the location of the proton. The latter two do not appear to be problems, since $\psi_H^1(Q_0)$ times the three-dimensional volume element is finite everywhere. The first singularity demands more care. Because of it, strictly speaking no integrals involving $\psi_H^1(Q_0)$ exist, but one can obtain principal values for the integrals if one is careful when integrating near the singularity to do so in a spherically symmetric fashion. One must be similarly careful in evaluating $E_H^1(R, Q_0)$, for the integrand here has the same bad infinity at the deuteron. (It is particularly easy in this

case to get a wrong answer.) These "conductionally convergent" integrals have been dealt with in a more general way by Pitzer [8].

When R is taken to zero in $\psi_H^1(Q_0)$, we obtain a result similar in form to that for $\psi_D^1(Q_0)$, as one would expect, but the two answers are not identical. Both solve eq. (8), the perturbation theory differential equation.

$\psi_H^1(Q_0)$ is not a priori orthogonal to the ground state, but with our choice of dipole moment operator this does not matter, as any component of $\psi_H^1(Q_0)$ proportional to the ground state will not contribute to $\langle \mu(Q_0) \rangle$.

With $\psi_H^1(Q_0)$ in hand we calculate μ_{III} , which is

$$\begin{aligned} \mu_{III} = & 4\{E_H^1(R, Q_0)\{\text{Ei}(2R) (\cosh R T_1 - \sinh R T_2) - e^{-R}[i \text{Ei}(2R) (T_1 + T_2) - T_3]\} \\ & - Q_0\{\text{Ei}(2R) (\cosh R S_1 - \sinh R S_2) + e^{-R}[i \text{Ei}(2R) (S_1 + S_2) - S_3]\}\} \end{aligned} \quad (26)$$

with

$$\begin{aligned} T_1(R) &= \frac{15}{8R} + \frac{R}{8}, \quad T_2(R) = \frac{15}{8R^2} + \frac{3}{4}, \quad T_3(R) = \frac{R^4}{120} + \frac{17R^3}{240} + \frac{13R^2}{48} + \frac{17R}{24} + \frac{15}{8} + \frac{15}{4R}, \\ S_1(R) &= \frac{R}{2} + \frac{55}{2R} + \frac{210}{R^3}, \quad S_2(R) = 5 + \frac{195}{2R^2} + \frac{210}{R^4}, \quad S_3(R) = 2R + \frac{95}{6} + \frac{235}{3R} + \frac{210}{R^2} + \frac{420}{R^3}, \\ E_H^1(R, Q_0) &= Q_0 \left[\frac{2}{R^3} - 2e^{-2R} \left(\frac{4}{3} + \frac{2}{R} + \frac{2}{R^2} + \frac{1}{R^3} \right) \right]. \end{aligned} \quad (27)$$

Using the right-hand sides of eqs. (21), (14), (26), and (13) in eq. (6) gives $\langle \mu(R, Q_0) \rangle$ explicitly.

3. A check: MO calculation of the induced field gradient

The error inherent in our usage of the MO approximation can be roughly quantified by consideration of a simplified version of a measurement of the Stark effect in a nuclear quadrupole resonance (NQR) experiment [9]. We imagine there exists a constant electric field of strength E directed along the internuclear axis of HD. It interacts indirectly via the electrons of the molecule with the nuclear quadrupole moment of the deuteron, and this interaction energy is given formally by

$$E(Q_0, E) = 2 \sum_{N \neq 0} \frac{\langle 0 | \mu E | N \rangle \langle N | q_D Q_0 | 0 \rangle}{E^{(0)} - E^{(N)}}, \quad (28)$$

where q_D is the electric field gradient operator evaluated at the deuteron. This is ordinarily a tensor, but we use a scalar notation because only the zz component of the tensor contributes. (This is because the electric field is directed along the z (internuclear) axis, and the molecule has cylindrical symmetry about that axis.) Furthermore, in this case $q_D Q_0 = Q_D$, as we have defined the latter in eq. (11), and the right-hand side of eq. (28) is then identical with the right-hand side of eq. (1) if we divide the former by E . We can interpret this energy as arising from induced moments in two complementary ways: Either $\langle q_D(E) \rangle$, an electric field gradient at the nucleus, resulting from an externally induced electronic dipole moment, interacts with the nuclear quadrupole moment Q_0 ; or $\langle \mu(Q_0) \rangle$, the electronic dipole moment induced by the nuclear quadrupole, interacts with the external field E .

Thus we will obtain exactly the same result if we calculate $\langle q_D(E) \rangle / E$ and $\langle \mu(Q_0) \rangle / Q_0$ by any exact method (or any one-electron approximation thereof that satisfies the Hellmann-Feynman theorem). If we use an approximate method to calculate them, the discrepancy between the two quantities can be looked upon as a rough guide to the accuracy of the method. Accordingly, we used our MO approach to calculate $\langle q_D(E) \rangle$ just as we did $\langle \mu(Q_0) \rangle$. The calculation proceeds in precisely the same manner. The equivalent of eq. (6), above, is

$$\langle q_D(R, E) \rangle = \frac{2}{1+S_0} \int d^3r [\psi_H^0 q_D \psi_H^1(E) + \psi_H^0 q_D \psi_D^1(E) + \psi_D^0 q_D \psi_H^1(E) + \psi_D^0 q_D \psi_D^1(E)] . \quad (29)$$

We have already calculated $\psi_H^1(E)$ (it is given by eq. (20) by setting $\mu_0=E$), and $\psi_D^1(E)$ is of exactly the same form. (This wavefunction is in ref. [10], p. 264.) The evaluation of the four integrals in eq. (29) is then straightforward.

4. Discussion

The solid line in fig. 1 shows our final result for $\langle \mu(Q_0) \rangle / Q_0$ plotted versus internuclear separation R . (Since we place the origin of our coordinate system at the proton, a positive $\langle \mu \rangle$ indicates a dipole moment in the sense H^-D^+ , a shift of electron density toward the proton.) The dashed line in fig. 1 shows our final result for $\langle q_D(E) \rangle / E$ plotted versus R . The vertical bar in fig. 1 indicates the equilibrium HD bond distance (1.402 atomic units). The value of the induced dipole moment at this separation is $0.075Q_0$ atomic units. Using for Q_0 the value of $0.002738 \times 10^{-24} \text{ cm}^2$ given by Ramsey [11], this corresponds to $1.9 \times 10^{-11} \text{ D}$. Integrating $\langle \mu(R, Q_0) \rangle$ over the ground-state vibrational wavefunction of HD gives an average dipole moment of $0.078Q_0$ atomic units, which is also about $1.9 \times 10^{-11} \text{ D}$ for Ramsey's Q_0 . The value of the induced field gradient at the equilibrium internuclear separation is $-0.094E$ atomic units.

Note the change in sign of the dipole moment as R gets larger. We offer a simple, intuitive (semantically loose) explanation of this sign change: The angular part of the quadrupolar potential field looks like a d_{z^2} orbital, with two positive lobes sticking out directly toward and away from the proton, and a negative donut-shaped lobe girdling the deuteron with the "hole" in the "donut" facing the proton. When R is big, the electrons

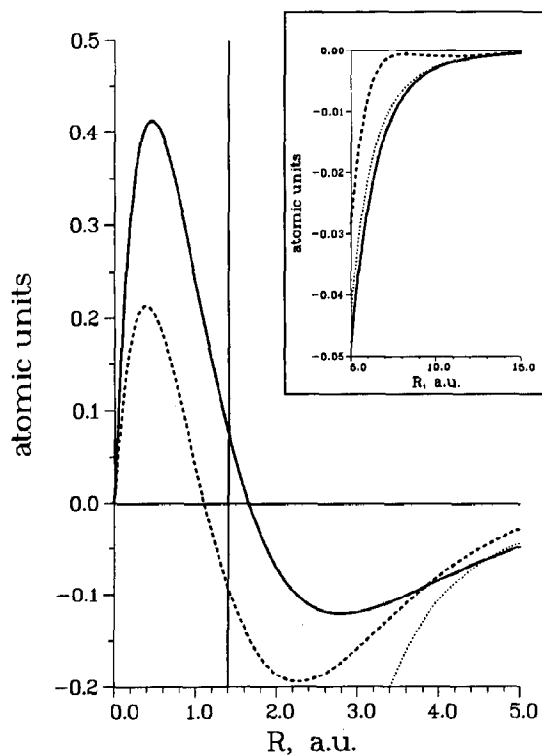


Fig. 1. Our calculations plotted versus internuclear separation, R , in atomic units: The solid line is the MO calculation of the quadrupole-induced dipole per unit quadrupole moment. The dotted line is the "ball and stick" calculation of the same quantity. The dashed line is the MO calculation of the induced electric field gradient at the deuteron per unit external electric field. The vertical bar indicates the equilibrium HD bond distance. At this distance the value of the induced dipole is about $0.075Q_0$ atomic units when calculated using the MO approach, and about $-7.0Q_0$ atomic units (and therefore below the graph) when calculated using the "ball and stick" model. The field gradient at this distance is $-0.094E$ atomic units. The inset shows the behaviour of the three functions at large R .

are primarily affected by the positive lobe of the quadrupole sticking out toward the proton. They therefore tend to remain closer to the deuteron than they would in the absence of the perturbation, leading to a negative dipole moment. At smaller R , however, the positive lobe is more of a "background" field, and the electrons are more affected by the negative lobe of the quadrupole, which looks roughly like a cone opening toward the proton. The electrons are then "squeezed" toward the proton, resulting in a positive dipole moment. In support of this interpretation we note that the sign change in the dipole moment is due solely to the term in our expression for the dipole moment which describes the dipole induced on an H atom by a naked quadrupole. (This is μ_1 , given by eq. (21).)

At internuclear separations, R , much larger than the size of the H atom, it is possible to treat this system with a "ball and stick" model, where we consider the H atom as a dielectric "ball" of uniform isotropic polarizability α and negligible radius, separated by a rigid "stick" of length R from another such "ball" representing the D atom. The electric field E produced by the quadrupole is $-\nabla Q_D$, which at the proton points along the internuclear axis towards the deuteron, and has magnitude

$$E = Q_0 \frac{\partial}{\partial R} \frac{2}{R^3} = -Q_0 \frac{6}{R^4}. \quad (30)$$

The magnitude of the dipole moment induced on the H atom "ball" by this electric field is then αE . The quadrupole induces no dipole on the D atom "ball" because of the spherical symmetry and the orthogonality of dipole and quadrupole moments. It is easily shown that the effect on the D atom "ball" of the induced dipole on the H atom "ball" is proportional to the ordinary H_2 overlap integral. This itself is proportional to e^{-2R} , and so for large R negligible. The polarizability of the H atom is known to be exactly $\frac{9}{2}$. (See, for example, ref. [10], p. 265). So the "ball and stick" model predicts that the total magnitude of the induced dipole moment on HD is

$$\langle \mu(Q_0) \rangle = -Q_0 \frac{27}{R^4}. \quad (31)$$

The result is plotted versus R as the dotted line in fig. 1. As you can see, our MO result approaches the "ball and stick" result asymptotically, as it must. (This can be seen algebraically by noting that when R is large, the only significant part of our result for $\langle \mu(R, Q_0) \rangle$ is the non-exponential, leading term of μ_1 , given in eq. (17), times $2/(1+S_0)$, where S_0 is the H_2 overlap integral. But S_0 is nearly zero, so the MO result gives at large R exactly the same algebraic expression for the induced dipole moment as does the "ball and stick" model.)

Note that the "ball and stick" model fails to predict the sign change in $\langle \mu(Q_0, R) \rangle$ at small separations that is predicted by the MO theory. At the equilibrium HD bond distance, for example, the dipole moment predicted by the "ball and stick" model is $-7.0Q_0$ atomic units, or -1.7×10^{-9} D – opposite in sign to the MO result. This sign difference is helpful, because unfortunately the magnitude of $\langle \mu(Q_0) \rangle$ is far too small to measure experimentally, and we must look for indirect evidence that our prediction is correct. We find some such evidence in the results of measurements made recently by Sleator et al. [12]^{#1} of the electric dipole moment induced by the ^{35}Cl nuclear quadrupole moment in the covalently bonded oxygen atoms in a single crystal of NaClO_3 . (This is the reciprocal to the NQR Stark effect experiment considered above.) These experimenters made estimates of the dipole moments they measured using a "ball and stick" model similar to that described above, but including the Sternheimer anti-shielding factor in Q_0 (see next paragraph). This model is certainly valid at large separations. But they found that in one case (that of the $Y_{\frac{3}{2}^2}$ components of the ^{35}Cl quadrupole) the induced dipole moment predicted was opposite in sign from that measured, indicating that the dipole moment induced at the small separations characteristic of the experiment was opposite in sign to that which would have been induced at much larger separations. This is an encouraging sign that the sign change in $\langle \mu(Q_0) \rangle$ that we predict actually exists.

^{#1} A fuller report of this effect will be published shortly by Sleator et al. [13].

The chief source of error in our approach is that it is a one-electron calculation, and so no shielding from the quadrupole of one electron by the other is treated. (Such shielding for quadrupolar interactions was first treated by Sternheimer [14].) However, as mentioned before, the factor in $\langle \mu(Q_0) \rangle$ responsible for the direction change in the moment, μ_1 , is that which describes a hydrogen atom perturbed by a naked quadrupole at a distance R . So we can get a rough idea of how the shielding that would appear in a many-electron calculation would affect our results by the following procedure: First, we calculate the electric potential due to a quadrupole inside an isolated deuterium atom. We write it as

$$Q'_D = Q_D [1 + S(r)], \quad (32)$$

where Q_D is, as before, the potential due to a *naked* quadrupole at the deuteron, and $S(r)$ is a function of the radial distance r from the deuteron. $S(r)$ is easily calculated for the deuterium atom. It is (in atomic units)

$$S(r) = \frac{4}{3} - \frac{16}{3} e^{-2r} \left(\frac{1}{15} r^4 + \frac{1}{3} r^3 + \frac{1}{2} r^2 + \frac{1}{2} r + \frac{1}{4} \right) - \frac{32}{15} r^4 e^{-2r} + \frac{32}{9} r^5 \text{Ei}(2r), \quad (33)$$

where the non-elementary function $\text{Ei}(2r)$ is defined in eq. (16) above. (The asymptotic limit of this function, $\frac{4}{3}$, is the usual Sternheimer anti-shielding factor γ_∞ . This is what would be used in a shielded ball and stick model, like that used by Sleator et al. [12,13].) Now in the key term μ_1 we substitute for Q_0 , the strength of the quadrupole, the expression $Q_0 [1 + S(R)]$, where R is the internuclear separation. This takes into account in an average way the shielding of the quadrupole by the deuterium electron. The result of such a calculation is, however, only a trivial change from the results shown in fig. 1. This gives us some confidence that our results would be qualitatively reproduced by a full many-electron calculation.

5. Conclusion

The discrepancy we see between $\langle \mu(Q_0) \rangle / Q_0$ and $\langle q_D(E) \rangle / E$ in fig. 1, taken as a rough indicator of the precision of our result, is why we give the magnitude of the induced dipole at the equilibrium separation to so few significant figures, although of course we could calculate it within the limits of the theory to arbitrary precision. Even the *direction* of the dipole moment at equilibrium is open to question, since this distance falls so close to where $\langle \mu(Q_0) \rangle / Q_0$ and $\langle q_D(E) \rangle / E$ change sign. We have no obvious reason to consider either of the two MO calculations a priori more accurate, and since they indicate opposite directions, we really cannot say in which direction the dipole moment points. However, we feel that the importance of this work is not in the actual value of the dipole moment at the equilibrium separation (which could be obtained with considerably greater accuracy via traditional numerical methods), but in the prediction of the *qualitative form* of the moment as a function of internuclear separation, as indicated in the two curves in fig. 1, and the insight this may give about experiments on much more complicated systems, such as the NaClO_3 experiments mentioned.

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