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The Effect of Molecular Vibrations on Apparent Bond Lengths

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A study is made of the apparent bond contraction in H_2^+ and H_2 which results from molecular vibration in the ground or first-excited mode, it being assumed that the positions of the two nuclei can be inferred from the positions of the corresponding peaks in the electron density determined by X-rays. It appears that a convolution model, in which we suppose that during the vibration the charge cloud near a nucleus moves with the nucleus and without change of shape, is good enough for most purposes. However, a full Born–Oppenheimer study of the changes in this charge cloud during vibration leads to bond contraction in the ground vibrational state of H_2^+ which is about $0{\cdot}124\ a_0$ instead of a convolution-model contraction of $0{\cdot}096\ a_0$. To get a satisfactory result it is necessary to have good wave functions, particularly in the neighbourhood of the nuclei.

1. Introduction

Recent very accurate experimental studies (Coppens, 1970; Dawson, 1970; Coulson, 1970; Jönsson & Hamilton, 1970) have shown that the centroid of the electronic charge around a given nucleus does not always coincide with the position of the nucleus as measured by neutron or electron diffraction (Jones & Lipscomb, 1969). It is easy to see that, in general, we should not expect coincidence of these two positions. For if $\mathbf{X}_i$ ($i=1, 2, \ldots n$) denotes the coordinates (spatial $\mathbf{r}_i$ and spin $\mathbf{s}_i$) of the n electrons, and $\mathbf{R}_j$ ($j=1, 2, \ldots N$) the positions of the N nuclei, the normalized molecular wave function† is $\Psi(\mathbf{X}_1, \ldots \mathbf{X}_n, \mathbf{R}_1, \ldots \mathbf{R}_N)$, leading to an electronic density

$$\begin{aligned}\varrho^{\text{elec}}(\mathbf{r}) &= n\varrho^{\text{elec}}(\mathbf{r}_1)\\ &= n\int \Psi\Psi^*\, ds_1\, d\mathbf{X}_2 \ldots d\mathbf{X}_n\, d\mathbf{R}_1 \ldots d\mathbf{R}_N \quad (1)\end{aligned}$$

and a nuclear density

$$\varrho^{\text{Nu}}(\mathbf{R}_1, \ldots \mathbf{R}_N) = \int \Psi\Psi^*\, d\mathbf{X}_1 \ldots d\mathbf{X}_n\,. \qquad (2)$$

Expression (1) describes the density inferred from X-ray measurements, and expression (2) the corresponding density inferred from neutron-diffraction measurements. Both density functions will have distinct peaks (assuming that in setting up the wave function we have kept the molecular centre of mass at rest); but the peaks will not necessarily be in identical positions. Thus the bond lengths as deduced by X-ray methods will not be quite the same as the bond lengths deduced by neutron diffraction.

In order to see how different effects contribute to these bond-length differences it is convenient to adopt the Born–Oppenheimer approximation for Ψ. This will be quite accurate enough for our purposes, and allows us to write, for a diatomic molecule

$$\Psi(\mathbf{X}_1, \ldots \mathbf{X}_n, R) = \Psi_R(\mathbf{X}_1, \ldots \mathbf{X}_n)\,\varphi(R) \qquad (3)$$

where we have used R to denote the internuclear distance, which also appears as a parameter in the normalized 'electronic wave function' $\Psi_R(\mathbf{X}_1, \ldots \mathbf{X}_n)$. The motion of the nuclei, which are supposed to oscillate with small amplitude around some equilibrium internuclear separation R_e, is governed by $\varphi(R)$; variations in $\Psi_R(\mathbf{X}_1, \ldots \mathbf{X}_n)$ as R varies will then indicate the extent to which the electronic charge cloud is itself modified during these vibrations. Since we are not concerned with anharmonic effects, we shall suppose that $\varphi(R)$ is adequately represented by an appropriate harmonic-oscillator wave function. Later, if we want to do so, we can superpose the anharmonicity variation of $\varphi(R)$. With these assumptions the nuclear density distribution (2) takes the form

$$\varrho^{\text{nuc}}(R) = \varphi^2(R)\,, \qquad (4)$$

and, for any fixed internuclear separation R, the electronic density distribution (1) takes the form

$$\varrho_R^{\text{elec}}(\mathbf{r}) = n\int \Psi_R^2(\mathbf{X}_1, \ldots \mathbf{X}_n)\, d\mathbf{s}_1\, d\mathbf{X}_2, \ldots d\mathbf{X}_n\,. \quad (5)$$

Finally, if we allow for the distribution (4) of bond length R, we obtain the 'exact' Born–Oppenheimer electron density

$$\varrho^{\text{elec}}(\mathbf{r}) = \int \varrho_R^{\text{elec}}(\mathbf{r})\,\varphi^2(R)\, dR\,. \qquad (6)$$

It is convenient to distinguish properties of the electron density which we may label as static and dynamic. By static we refer to the character of $\varrho_R^{\text{elec}}(\mathbf{r})$ when the nuclear coordinates are kept fixed at the equilibrium value $R=R_e$. In such a case we are discussing $\varrho_{R_e}^{\text{elec}}(\mathbf{r})$. By dynamic we refer to those characteristics of $\varrho^{\text{elec}}(\mathbf{r})$ which are the result of the motion of the nuclei. In

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† For molecular crystals a small elaboration is necessary, but we shall disregard this.

such a case our interest lies chiefly in the role of $\varphi^2(R)$ in (6).

The static electron density has already been discussed by Coppens & Coulson (1967) and Coulson (1970). There it is shown that since electrons engaged in the formation of a covalent bond between two atoms are preferentially drawn into the region between the nuclei, thus leading to a bond-charge, the electron density around either nucleus is not symmetrical with respect to the nucleus. Thus the centroid of the charge associated with either atom lies a little distance away from the nucleus in the direction of the other atom. The result is an apparent shortening of the bond length. Such shortening will necessarily be greatest if there are very few inner-shell non-bonding electrons, since these latter will be centred around the nucleus. This type of X-ray shortening will therefore be largest for bonds to a hydrogen atom, where apparent contractions of the order of 0·2 Å are known (Hamilton & La Placa, 1968; Jönsson & Hamilton, 1970). However, when there are lone-pair electrons around an atom their condition of orthogonality to the bonding electrons will result in a polarization in the opposite direction. Coppens & Coulson (1967) showed that for a terminal nitrogen atom the lone-pair effect was greater than the bond effect, so that now X-ray measurements would lead to an apparent increase in bond length of about 0·04 Å. This fitted well with some careful studies of the crystal structure of hexamethylenetetramine (Duckworth, Willis & Pawley, 1969) where no difference appeared in the X-ray and neutron-diffraction determinations of the positions of the carbon atoms, but the X-ray determination of the positions of the nitrogen atoms placed them 0·018 Å further out from the rest of the molecule than did the neutron-diffraction measurement. This is clearly due to the presence of lone-pair electrons around the nitrogen atom, but not around the carbon atom.

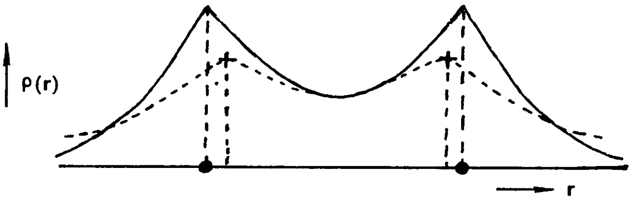

Fig. 1. Axial charge density in H_2 (schematic) (after Coulson, 1970). ——— static density when $R=R_e$, ------- dynamic density taking account of nuclear vibration. The crosses mark 'apparent' positions of nuclei.

Our main concern in the rest of this paper will be with the dynamic effect that results from the motion of the nuclei. We shall consider two ways of dealing with this effect. In the first, which we call the convolution method, we suppose that the nuclear vibrations are so small that the shape of the charge cloud close to the nucleus does not change during a vibration. This means that we suppose the nucleus to 'carry' all the charge density near it without change of shape. This is equivalent to supposing that, in (6), $\varrho_R^{\text{elec}}(\mathbf{r})$ is to be given its value when $R=R_e$, and that $\mathbf{r}$ is then measured relative to the position of the nucleus. Furthermore we take for $\varphi(R)$ the appropriate harmonic-oscillator wave function. In the second procedure we introduce the correct form of $\varrho_R^{\text{elec}}(\mathbf{r})$ at all R and then complete the integration. The advantage of the first method, which is less accurate than the second, is that it is easier, and only requires a knowledge of the electronic wave function at the equilibrium distance R_e. We shall show that the error introduced by using this approximation is small enough to be unimportant in nearly every case.

In this first study our calculation will be limited to H_2^+ and H_2, in both of which, due to absence of any electrons other than those involved in bonding, and to the larger amplitude of vibration, we expect larger effects than for heavier nuclei; but we hope in a later paper to consider other systems. A further reason for studying the hydrogen molecule and ion is that a large range of calculations of molecular wave functions is available, so that we can more easily study the effect of good or bad wave functions and more confidently pass on to consider more complicated molecules for which fewer wave functions are available (and none of them as good as the best for hydrogen). In this way we can show that the quality of the wave function is important, particularly near the nucleus.

There is one more feature to mention, which is of general interest. Since the electron–nuclear attraction term in the Hamiltonian is of the form Z_k/r_{ki}, where r_{ki} is the distance of electron i from nucleus k, which carries charge $+Z_k$, it follows (Kato, 1957; Steiner,

Table 1. *Molecular constants*

		H_2^+	H_2	
		Bates wave function	Wang wave function	'Natural' orbital expansion
Internuclear separation	R_e(a.u.)	2·0	1·406	1·4009
	ω_e(cm^{-1})	2297	4395·24	4395·24
Zero-point energy	E_0(cm^{-1})	1133	2227	2227
Classical amplitude of one nucleus (with energy E_0)	A_0(a.u.)	0·1602	0·11739	0·11739
Vibration constant	γ(a.u.)	9·60833	18·3853	18·3853
Orbital exponent	α	—	1·166	0·995

The data come from Herzberg (1950) or are computed from data from Herzberg.

1963; Bingel, 1967) that there is a cusp at each nucleus. At any nucleus the gradient of Ψ is discontinuous. For an isolated atom it is obvious that $\partial\Psi/\partial r$ has spherical symmetry. But for an atom in a molecule, due to the disturbance of central symmetry, this is no longer the case. In the cases of H_2^+ and H_2 the charge density falls off more rapidly on the far side of the molecule than between the nuclei. It follows that the result of molecular vibration will be to smooth out the cusps, and lead to a peak in charge density lying between the two nuclei, as is shown schematically in Fig. 1, taken from Coulson (1970). The magnitude of this effect has never hitherto been calculated; we present the results of such a calculation now. However, it should be pointed out that bond shortenings due to crystal thermal motion have been calculated by Tomiie (1958) for C–H bonds using a convolution approximation.

2. Validity of the convolution approximation

If we adopt the convolution approximation we may write equation (6) in the form

$$\varrho^{\text{elec}}(\mathbf{r}) = \int \varrho_{R_e}^{\text{elec}}(\mathbf{r}-\mathbf{t})\, \varphi^2(\mathbf{t})\mathrm{d}\mathbf{t} \qquad (7)$$

We have evaluated this integral for H_2^+ and for H_2. The constants needed for the harmonic-oscillator functions φ are taken from Herzberg (1950), and are summarized in Table 1. In these calculations we consider only the lowest (zero-point) vibrational level.

In the case of H_2^+ we can use effectively accurate wave functions by choosing those obtained by Bates, Ledsham & Stewart (1953) in terms of spheroidal coordinates λ, μ. For the $1s\sigma$ ($1\sigma_g$) state the wave function is

$$\begin{aligned} \Psi_R(\lambda,\mu) &= L(\lambda)\, M(\mu), \text{ where} \\ L(\lambda) &= (\lambda+1)^\sigma \exp(-\varrho\lambda) \sum_{t=0}^{2} g_t \left(\frac{\lambda-1}{\lambda+1}\right)^t \\ M(\mu) &= \sum_{s=0}^{5} F_{2s}P_{2s}(\mu)\,. \end{aligned} \qquad (8)$$

$P_{2s}(\mu)$ is the Legendre polynomial of order $2s$, and numerical values are provided for the parameters σ, ϱ, F_{2s} and g_t. In the convolution approximation we adopted the value $R_e = 2{\cdot}0\ a_0$: in the exact Born–Oppenheimer approximation we used the parameter values tabulated by Bates *et al.*, and interpolated for the internuclear distances needed by a six-point Legendre formula. The results are shown in Fig. 2, which also shows the static density $\varrho_{R_e}^{\text{elec}}(\mathbf{r})$. The difference between the convolution curve and the exact curve is small; both are very different from the static curve. This diagram shows very clearly how the result of molecular vibration is to reduce the maximum density and smooth out the cusp.

For H_2 we have used a simple Wang (1928) type of wave function, where

$$\Psi_R = \{\Psi_a(\mathbf{r}_1)\, \Psi_b(\mathbf{r}_2) + \Psi_b(\mathbf{r}_1)\, \Psi_a(\mathbf{r}_2)\}/[2(1+S^2)]^{1/2} \qquad (9)$$

and Ψ_a, Ψ_b are screened hydrogenic orbitals around the nuclei A and B, and having the form

$$\Psi_a = (\alpha^3/\pi)^{1/2} \exp(-\alpha r_a)\,. \qquad (10)$$

S is the usual overlap integral $\int \Psi_a \Psi_b\, \mathrm{d}\tau$. The orbital exponent α varies with internuclear distance. In the convolution approximation we took $R_e = 1{\cdot}406\ a_0$ and $\alpha = 1{\cdot}166\ a_0^{-1}$: in the exact Born–Oppenheimer approximation we used values of α calculated by one of us (Coulson, 1937), and interpolated with a five-point Legendre formula. In both the H_2^+ and H_2 cases the necessary quadratures were performed by a Romberg method, with Richardson extrapolation. The final results for H_2 are shown in Fig. 3.

It follows from Figs. 2 and 3 that if an accurate X-ray measurement is made of the electron density, and the peak values are taken to be the positions of the nuclei, there will be an apparent shortening of the bond length. For both H_2^+ and H_2 this shortening is slightly larger for the exact Born–Oppenheimer approximation than for the convolution approximation. Thus for H_2^+ the two shortenings are $0{\cdot}124\ a_0$ and $0{\cdot}096\ a_0$. This is of the magnitude often supposed to apply to bonds involving hydrogen. It is large in relation to the precision now available from good X-ray and neutron-diffraction experiments.

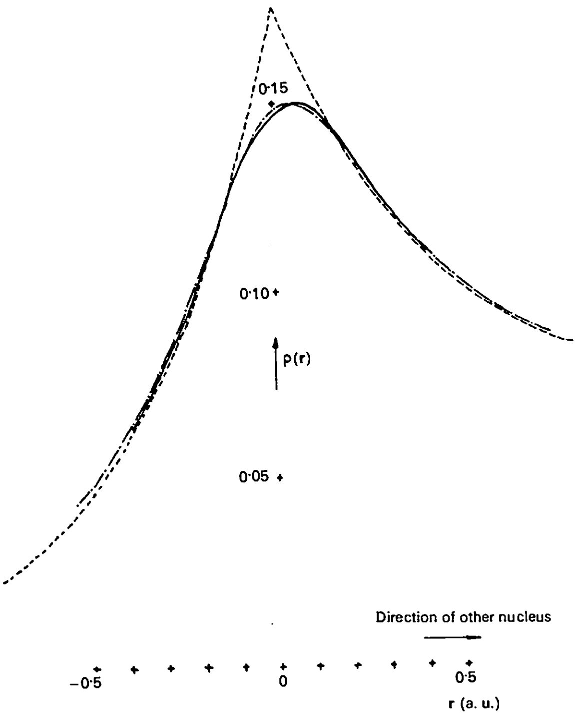

Fig. 2. Axial charge density for H_2^+. -------- static density when $R = R_e$, ——— dynamic density (Born–Oppenheimer approximation), -·-·-·-· dynamic density (convolution approximation).

3. Dependence of shift on quality of wave function

In the case of H_2^+ we have studied the effect of using different vibrational wave functions. In particular we have used

(i) the lowest vibrational mode

$$\varphi^2(t)=2\sqrt{(\gamma/\pi)}\exp\{-4\gamma t^2\} \tag{11}$$

(ii) the first-excited vibrational mode

$$\varphi^2(t)=16\gamma\sqrt{(\gamma/\pi)}\,t^2\exp\{-4\gamma t^2\} \tag{12}$$

(iii) the classical distribution function for the lowest vibration (with correct zero-point energy)

$$\varphi^2(t)=(1/\pi A_0)\{1-(t/A_0)^2\}^{-1/2} \tag{13}$$

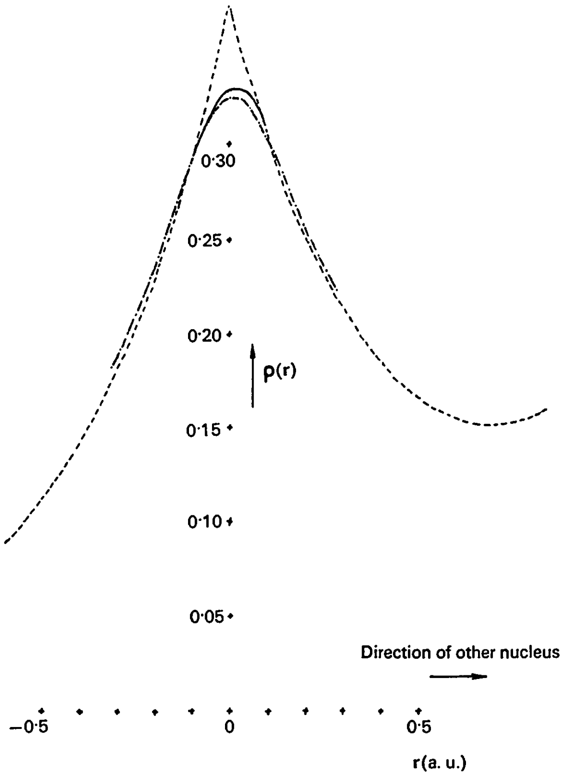

Fig. 3. Axial charge density for H_2 – Wang wave function. -------- static density when $R=R_e$, ——— dynamic density (Born–Oppenheimer approximation), -------- dynamic density (convolution approximation).

where, in all three cases, $t=(R-R_e)/2$ denotes the displacement of any one atom from its mean position. Our calculations in §2 suggested that we could reasonably safely use the convolution approximation, and so, on account of its simplicity, we have done so. The necessary constants A_0 and γ are given in Table 1, and the final results in Fig. 4.

As would be expected the extent of bond shortening increases markedly with increase in vibrational quantum number. This would imply a temperature effect. The actual displacements deduced from Fig. 4 are listed in Table 2. It can be seen that the classical distribution, by giving greatest weight to the end-points of the vibrations, overestimates the bond-shortening.

We turn to neutral H_2. The most appropriate wave function to use is that of Davidson & Jones (1962), who deduced the 'natural orbitals' as eigenfunctions of the first-order density matrix derived from the fifty-term expansion of Kolos & Roothaan (1960). Each such natural orbital is a known linear sum of fifteen terms, each of which is of the form (in spheroidal coordinates λ, μ, φ)

$$\lambda^n\mu^j(\lambda^2-1)^{m/2}(1-\mu^2)^{m/2}\exp(-\alpha\lambda)\exp(im\varphi)\,.$$

The values of α and R_e are shown in Table 1. Davidson & Jones have shown that ten of these natural orbitals lead to a total electron density essentially the same as in the full wave function of Kolos & Roothaan. With these natural orbitals it is a simple matter to compute $\varrho^{\text{elec}}_{R_e}(\mathbf{r})$, and hence $\varrho^{\text{elec}}(\mathbf{r})$.

Fig. 5 shows the results obtained, in each case adopting the convolution approximation. First there is the static density $\varrho^{\text{elec}}_{R_e}\mathbf{r})$, and then the dynamic density with the three nuclear distributions (11)–(13) similar to those previously used for H_2^+. The displacements of the maximum values of the density are given in Table 2, together with those for H_2^+.

The curves in Figs. 2–5 allow us to compare the results that follow from the use of good or bad quality wave functions. Thus, for H_2 the Wang function leads to a static density which is almost symmetrical around each nucleus, and therefore to a bond shortening which is too small. The asymmetry around each nucleus is closely connected to the build-up of charge in the overlap region between the nuclei. All Heitler–

Table 2. *Displacements of the maximum of the 'static' electron density in the convolution approximation*

The origin is taken at atom *a*; all shifts are in the direction of atom *b*; units are a.u.

	Molecule		
	$H_2{}^+$	H_2	
Nuclear distribution functions	Bates wave function	Wang wave function	'Natural' orbital expansion
Zero-point vibration	0·048 (0·096)	0·01 (0·02)	0·04 (0·08)
Classical distribution (with zero-point energy)	0·09 (0·180)	—	0·07 (0·14)
First-excited vibration	0·164 (0·328)	—	0·120 (0·240)
Equilibrium distance	$R_e=2{\cdot}00$	$R_e=1{\cdot}406$	$R_e=1{\cdot}4009$

Note: The figure in brackets is the total change in the internuclear separation.

London type functions tend to underestimate this bond charge (Roux, Besnainou & Daudel, 1956). This is probably related to the fact that with wave function (9) the bond charge has a magnitude

$\frac{2S}{1+S^2}\,\Psi_a(\mathbf{r})\,\Psi_b(\mathbf{r})$, whereas the corresponding simple molecular-orbital function leads to a value $\frac{2}{1+S}\,\Psi_a(\mathbf{r})\,\Psi_b(\mathbf{r})$. The ratio of these numbers is $\frac{S(1+S)}{(1+S^2)}$, with a value about $\frac{2}{3}$ for the ground state of H_2. Thus the Heitler–London wave function leads to less asymmetry of the static density, and so to a reduced apparent bond shortening. Since the Davidson–Jones density may be taken to be effectively exact, this means that a valence-bond function, while giving a better total energy, gives a poorer description of bond contraction than does the corresponding molecular-orbital function. This is another example of the conclusions of Mukherji & Karplus (1963), that two approximate wave functions, even if they lead to similar (and good) energies, may nevertheless give quite different one-electron densities.

A comparison of the static densities in Figs. 2 and 5 shows that in H_2 the asymmetry at the nucleus is nearly as prominent as in H_2^+. This seemed to us at first to be rather surprising.

Another initially surprising result is the very unsymmetrical shape of the dynamic density $\varrho^{\text{elec}}(\mathbf{r})$ shown in Figs. 4 and 5 for the first-excited vibrational state. It is almost as if there were a tendency to have two peaks and not one around each nucleus. Since this situation is found in both the ion and the neutral molecule, it is probably not spurious. Indeed its explanation seems to be that for the first-excited state the nuclear distribution function (12) has zero value at $t=0$, and has two peaks on either side at $t=t_0\equiv\pm(4\gamma)^{-1/2}$. With a completely symmetrical static density $\varrho^{\text{elec}}_{R_e}(\mathbf{r})$ this would naturally lead to two peaks in the dynamic density; but if the static density is markedly asymmetric, as happens with these two systems, the peak farthest away from the other nucleus is reduced in magnitude, and becomes a broad shoulder on the other peak. Confirmation of this comes from the agreement between the values of $2t_0$ and the separation between the peak and the shoulder in Figs. 4 and 5. For H_2^+ the values are both 0·32; and for H_2 the separation is 0·22 to be compared with $2t_0=0{\cdot}23$. It is interesting to note from Fig. 4 that the classical distribution function (13) for the ground state which has two peaks at $t=\pm A_0$ but a non-zero value at $R=R_e$, leads to a dynamic density showing only a small shoulder on the far side of the nucleus. It is clear that in this kind of work it is not sufficiently good to use the classical distribution function. We must employ the correct quantum-mechanical one.

4. Conclusions

Since we have only considered H_2^+ and H_2 it would be dangerous to draw any very general conclusions. However, since the apparent bond shortening is related to the overlap density between the nuclei, the contribution that comes from the bonding pair of electrons is likely to be more important for covalent bonds than for largely ionic ones, where, in addition, there will usually be a lone-pair effect in the opposite direction. We are at present investigating this matter.

It is clear from our work that the error which results from using the convolution model is less than that which may arise from inadequate wave functions. It is particularly important to have these accurate near the nuclei. In this respect there is a close parallel with the calculations of the electric field at a nucleus, and other quantum-mechanical mean values involved in microwave studies. For if we write the static density near a nucleus in the approximate form

$$\varrho(\mathbf{r})=A\exp(-kr)+Br\cos\theta\exp(-k'r)$$

the asymmetry is wholly due to the second term, and the apparent bond shortening will be roughly proportional to the coefficient B. But this form of $\varrho(\mathbf{r})$ leads to an electrostatic potential consisting of a spherical term proportional to A and a non-spherical term proportional to $Br\cos\theta$. Thus the electrostatic field at the nucleus is also proportional to B, and so are mean-values such as $\langle\varrho\cos\theta/r^2\rangle$.

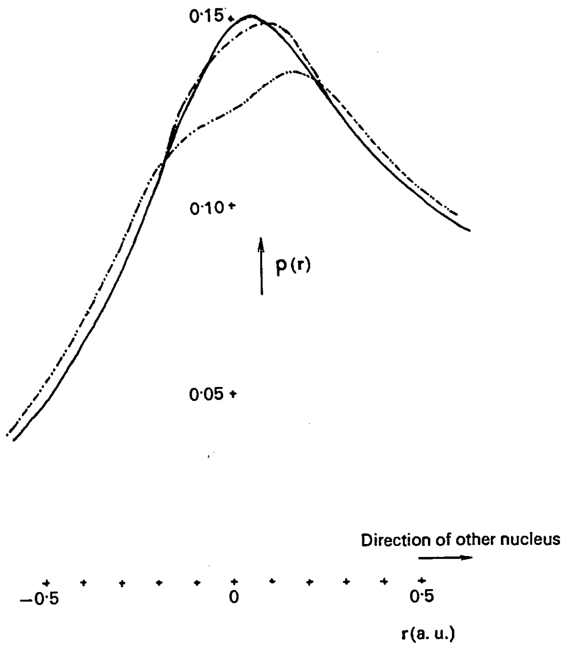

Fig. 4. Axial charge density for H_2^+. ——— dynamic density, lowest vibrational state (quantum theory distribution of R), - - - - - - - dynamical density, lowest vibrational state (classical distribution of R), -·-·-·-·- dynamic density first-excited vibrational state (quantum theory distribution of R).

In conclusion we should draw attention to a further point revealed by our analysis and where the usual X-ray techniques may lead to an error in the estimated bond lengths. We refer to the atomic scattering factors assumed for bonded hydrogen atoms. The electronic charge around a hydrogenic nucleus is both contracted and polarized. Each of these will affect the scattering factors to be used, and render invalid the use of these factors as calculated for a non-bonded atom. Stewart, Davidson & Simpson (1965) have shown that the first of these effects leads to an atomic scattering factor larger than that for an isolated hydrogen atom. If the isolated form factors are used abnormally low temperature factors may be found. These authors computed the 'best' spherical electron density around a nucleus that would fit the theoretically calculated molecular charge density. They used this to infer the corresponding form factor, and deduced an apparent displacement of the nuclei into the bond for a non-vibrating hydrogen molecule amounting to 0·14 Å. They did not, however discuss the effect of electronic asymmetry: in this respect the only calculations of which we are aware are those of McWeeny (1951, 1952, 1953, 1954) who considered the asymmetry resulting from hybridizing action among atomic *s* and *p* orbitals. In our present calculations of course both the contraction and polarization effects are implicitly taken account of in the use of accurate wave functions.

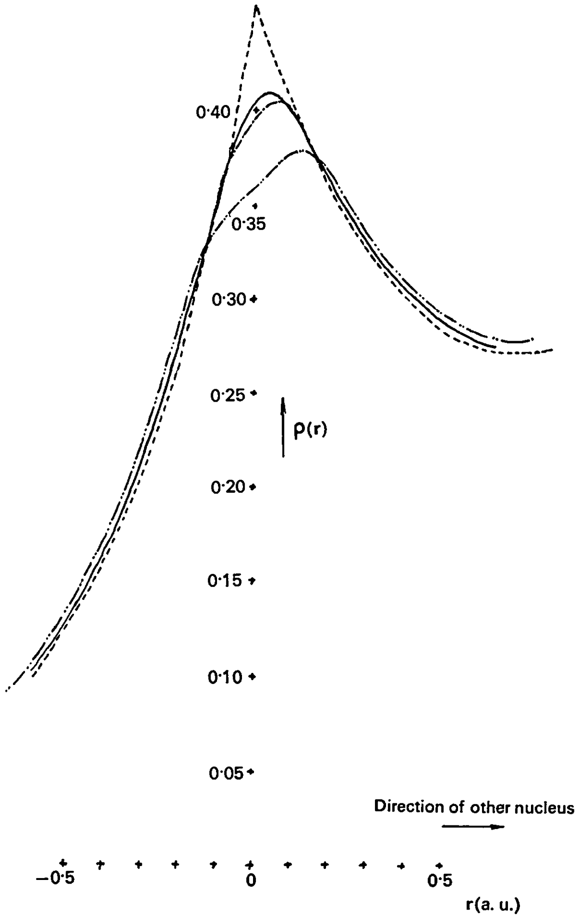

Fig. 5. Axial charge density for H_2. -------- static density when $R=R_e$, ——— dynamic density, lowest vibrational state (quantum theory distribution of R), ········ dynamic density, lowest vibrational state (classical distribution of R), -·-·-·- dynamic density, first-excited vibrational state (quantum theory distribution of R).

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