

**WALSH DIAGRAMS AND THE HELLMANN–FEYNMAN THEOREM:
A TRIBUTE TO THE LATE PROFESSOR CHARLES A. COULSON, F.R.S.
(1910–1974)**

Brian O'LEARY

*Department of Chemistry, University of Alabama at Birmingham, Birmingham,
Alabama 35294, USA*

and

R.B. MALLION

The King's School, Canterbury, Kent CT1 2ES, U.K.

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1. Introduction

It may come as something of a surprise to many of those who knew him to realise that Professor Charles Alfred Coulson, F.R.S. died as long ago as January 7th, 1974. Because we believe that his significance to chemistry in general, and to mathematical chemistry in particular, cannot be overstated, it would seem appropriate to remind the chemical public of this exemplary scientist in some suitable fashion. Customarily, this has been done by an outline of career and, in Professor Coulson's case, by citing his many contributions to British and international life – both inside and outside the academic world. However, since this has already been done successfully and extensively (see, for instance, refs. [1,2]), we shall try instead to convey here something of the spirit of the man and, as so many of us well remember, the unique flavour he gave to chemistry. To do this, we return to the Oxford of the early 1970's and "eavesdrop" on some of the highlights of his Physical Chemistry Laboratory lecture of March 2nd, 1971. The lecture was entitled "A New Way of Looking at Walsh's Rules for Molecular Geometry", and was tape-recorded by B. O'Leary with Professor Coulson's permission. R.B. Mallion took copious notes during the lecture, and Mrs. Coulson kindly supplied the slides used in the lecture. It was thus possible to reconstruct this lecture several years later by a process identical to that we adopted to produce the book *Hückel Theory for Organic Chemists* [3].

2. Highlights of the lecture

Professor Coulson began his lecture in characteristic style by saying: "It was in 1953, I think, that Walsh introduced what we now call Walsh's rules, in a series of about half a dozen papers which occupied a large amount of space in one of the issues of the *Journal of the Chemical Society* [4]. The intention was to rationalise, as far as it was possible to do so, the shapes of polyatomic molecules, not only in the ground state, but in excited states." Coulson then went on, by way of illustration, to consider triatomic molecules of the form AB_2 having between four and six valence electrons. He pointed out that, upon excitation, linear molecules become bent and that bent molecules become less bent. He then chose the diagram that Walsh himself

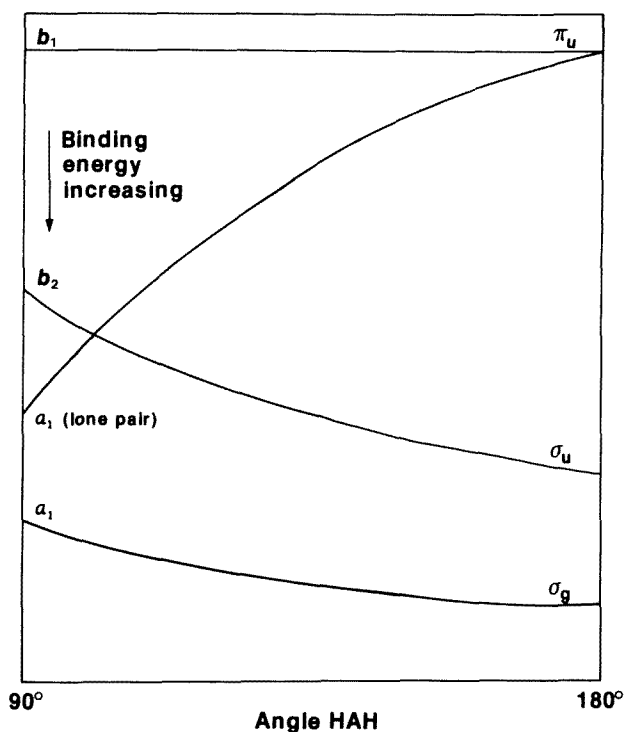


Fig. 1. The Walsh diagram for the AH_2 species. (Redrawn, with permission, from ref. [4].)

had drawn [4] of AH_2 (with C_{2v} symmetry) as providing the simplest vehicle for the ideas he was about to present. This diagram, which we reproduce in fig. 1, has been described by Mulliken as a correlation diagram. The diagram shows how individual orbital energies vary as the H-A-H valence angle changes from 90° to its 180° value in a linear molecule. Thus, an electron in a $1a_1$ molecular orbital (MO) will have lower energy – and, hence, better binding – if the valence angle increases. Although the

same is true for an electron in $1b_2$, precisely the opposite is found for $2a_1$. An electron in $1b_1$ (a π -orbital on the atom A), on the other hand, has little effect on the valence angle because the π -electron in question will be localised on A.

We are now faced with the question of the precise meaning of the *ordinate* in such diagrams, which Walsh called the "binding energy" of an MO. Coulson: "In his mind, I am pretty sure that he had the idea that he was really talking about ionisation potentials, but he never explicitly stated that this was the case." Efforts to identify this ordinate have proceeded along two lines [5–7]: on the one hand, trying to relate the Walsh ordinate to the LCAO-MO-SCF energy [8] and, on the other, seeking a one-electron MO energy that is genuinely additive, in order to relate it to total electronic energy [6,9–13]. Coulson: "A.H. Neilson and I had a go at this [11]. I am afraid the effect was so disastrous on Neilson that he has now become an explorer and is to be found normally at or near the North or South Pole! . . . [Laughter]. It is not clear whether the Walsh ordinate does or does not include nuclear repulsion. His arguments were very ambivalent ones – naturally enough, I think, at that stage Walsh is cagey about this. I contacted him and he says that he would rather not say whether the nuclear energy is or is not included So, admitting the difficulty of knowing exactly what it was that Walsh was talking about, we can see that a diagram of this sort, and other ones, of course, with other types of molecules, could really be quite useful."

"Well, this is the position, more or less, and it does suggest that one might try to see if it is possible to have another look at this problem from a rather different angle. The feature that is common to all of the previous treatments [4–13] is a discussion of the *energy*; the curves you plot are finally *energy* of some sort. Maybe you don't know what sort, but at least you know it's *energy*."

"Well, there is another way of approaching the stability of molecules, and that is through *force* rather than through energy. The idea goes back quite a long way (e.g. [14]) Before we come to a way in which you could do that, we might ask how you could hope or expect to get a *force*. Everybody knows how to get the energy, because that turns out to be obtainable from the Schrödinger equation. But we are going to get the force by another route and that is by use of the Hellmann–Feynman theorem. The Hellmann–Feynman theorem is a theorem of great beauty but not perhaps always as much utility as one might have hoped it would have."

"May I spend a minute on the Hellmann–Feynman theorem, a kind of interpretation [15]? Let me suppose that the Hamiltonian for any bond I am dealing with contains the usual sorts of differentiations etc., but also contains some *parameter* λ – i.e. $H(\lambda)$. I don't need to state at the moment what that parameter is. I shall take it to be a bond length or bond angle or something of that sort in due course." At this stage, Coulson supposed that the system in question is described by a wave function $\Psi(\lambda, \mathbf{x})$ dependent upon the parameter λ as well as the usual coordinates \mathbf{x} . He continued: "Now, associated with that wave function will be the energy $E(\lambda)$,

which itself must be dependent upon λ ." The following argument was then advanced: If Ψ be taken as normalised (i.e. $\int \Psi^* \Psi d\tau = 1$), the ordinary Rayleigh expression has denominator of unity, and so becomes

$$E(\lambda) = (\Psi, H\Psi). \quad (1)$$

This requires that Ψ shall be an exact wave function (i.e. $H(\lambda)\Psi = E\Psi$); in that case, we can differentiate with respect to λ to find how the energy varies with λ and thus obtain (e.g. [15,16]):

$$\begin{aligned} \frac{\partial E}{\partial \lambda} &= \left(\frac{\partial \Psi}{\partial \lambda}, H\Psi \right) + \left(\Psi, H \frac{\partial \Psi}{\partial \lambda} \right) + \left(\Psi, \frac{\partial H}{\partial \lambda} \Psi \right) \\ &= E(\lambda) \left\{ \left(\frac{\partial \Psi}{\partial \lambda}, \Psi \right) + \left(\Psi, \frac{\partial \Psi}{\partial \lambda} \right) \right\} + \left(\Psi, \frac{\partial H}{\partial \lambda} \Psi \right) \\ &= \left(\Psi, \frac{\partial H}{\partial \lambda} \Psi \right) \\ &= \left\langle \frac{\partial H}{\partial \lambda} \right\rangle. \end{aligned} \quad (2)$$

Coulson: "So . . . the rate of change of the energy with respect to the parameter λ is equal to the mean value of $\partial H/\partial \lambda$. Well then, if I know what parameter I have taken – a distance, an angle, or whatever it is – and if I can work out what $\partial H/\partial \lambda$ comes to, and evaluate the mean value, I have got $\partial E/\partial \lambda$ which, in this case, would be the *force*."

"As I have set it out, that is the theorem in the case that the wave function is an exact one. Well, of course, there are no exact ones in chemistry, so you might argue on those grounds that this is of no use. However, it has the advantage that if the system is a closed-shell one, and I use a genuine Hartree-Fock wave function, then the theorem is *still* true [15]. I can't then prove it as I did above – it's quite a different matter to prove it then – but the result *is* still valid [15]. Therefore, insofar as I can get exact or pretty good approximations to the Hartree-Fock wave function, then, in that sense, it *is* possible to get $\partial E/\partial \lambda$, to get force, and, perhaps, by integration, to get the energy."

"Well, how does that come in? Let me take a diatomic molecule A-B" (fig. 2). Coulson then gave the appropriate Hamiltonian for this many-electron system, in terms of the usual convention and the quantities shown in fig. 2, as

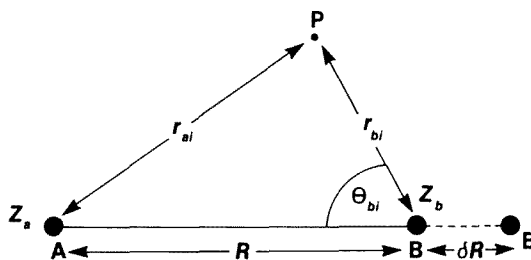


Fig. 2. Schematic representation of the AB molecule. Atoms A and B bear nuclear charges Z_a and Z_b , respectively, and are separated by a distance R , P is the position of the i th electron, distance r_{ai} from A and r_{bi} from B. θ_{bi} is angle PBA. Subsequently, A stays fixed and B moves a distance δR to B'.

$$H = \sum_{\text{electrons } i} -\frac{1}{2} \nabla_i^2 - Z_a \sum_{\text{electrons } i} \frac{1}{r_{ai}} - Z_b \sum_{\text{electrons } i} \frac{1}{r_{bi}} + \left(\sum_{i < j} \frac{1}{r_{ij}} \right) + \frac{Z_a Z_b}{R}. \quad (3)$$

Coulson then continued: "Now let me regard this distance R as the parameter. We have to watch out! In fact, confusion was caused here and I have to confess to being myself largely responsible for it! What is necessary is that we are absolutely certain which of r_{ai} and r_{bi} is varying, and for what reason. There are mistakes in the literature because it has not always been realised that the coordinates upon which R implicitly depends needed to be differentiated. Well, now we are going to suppose that R varies in such a way that B moves a distance δR to B' along the line A-B (fig. 2). Then, if I have an electron at point P, it remains at point P in the process of this differentiation. Well, if it is the i th electron we are talking of, what will change will be the distance r_{bi} ; r_{ai} will not change – nor, mercifully, will r_{ij} change." (r_{ij} being the distance between electron i and electron j .) Coulson then concluded that in the calculation of $\partial H/\partial R$, no contribution arises from the "troublesome" term – the electron interaction term – since coordinates of P, the position of the i th electron, are not changed – i.e. all electronic positions are *frozen*. Thus,

$$\begin{aligned} \frac{\partial H}{\partial R} &= -Z_b \sum_{\text{electrons } i} \frac{\partial}{\partial R} \left(\frac{1}{r_{bi}} \right) - \frac{Z_a Z_b}{R^2} \\ &= -Z_b \sum_{\text{electrons } i} \frac{\cos \theta_{bi}}{(r_{bi})^3} - \frac{Z_a Z_b}{R^2}, \end{aligned} \quad (4)$$

the second form of the first term being obtained after some manipulation, and the second term arising as a consequence of the inverse-square law of force between the nuclei. The Hellmann-Feynman theorem [in the form of eq. (2)] may now be applied to $\partial H/\partial R$ in eq. (4) to give

$$\frac{\partial E}{\partial R} = \left\langle -Z_b \sum_{\text{electrons } i} \frac{\cos \theta_{bi}}{(r_{bi})^3} - \frac{Z_a Z_b}{R^2} \right\rangle; \quad (5)$$

since $Z_a Z_b/R^2$ does not depend on the electronic wave function, its mean value is itself. Thus, eq. (5) may be written:

$$\begin{aligned} \frac{\partial E}{\partial R} &= -\frac{Z_a Z_b}{R^2} - \left\langle Z_b \sum_{\text{electrons } i} \frac{\cos \theta_{bi}}{(r_{bi})^3} \right\rangle \\ &= -\frac{Z_a Z_b}{R^2} - Z_b \int \Psi^* \left(\sum_{\text{electrons } i} \frac{\cos \theta_{bi}}{(r_{bi})^3} \right) \Psi \, d\tau \\ &= -F_B, \end{aligned} \quad (6)$$

where F_B is the force on atom B. This is equivalent to talking about charge density and, once charge densities have been obtained, the situation may be looked at from the point of view of classical electrostatics, eq. (6) being rewritten as

$$\frac{\partial E}{\partial R} = -\frac{Z_a Z_b}{R^2} - Z_b \int \frac{\rho \cos \theta_{bi}}{(r_{bi})^2} \, d\tau. \quad (7)$$

Here, with a simple determinantal wave function – a molecular-orbital determinantal wave function, say – ρ is the sum of contributions from each electron; that is,

$$\rho = \sum_{\text{electrons } i} \rho_i, \quad (8)$$

ρ_i being an electron density due to electron i . However, to know ρ satisfactorily, a good quality wave function is required. Still, we “. . . have got something that is genuinely additive [eq. (6)] . . . and . . . there is no question . . . about what one ought to plot.”

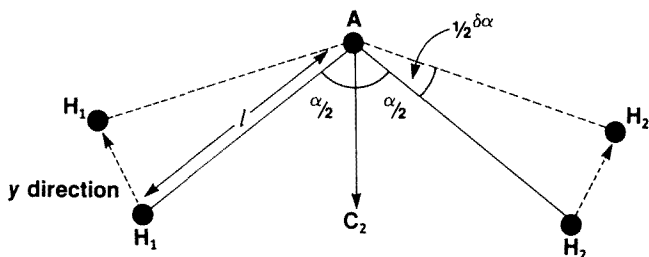


Fig. 3. Symmetric bending of an AH_2 molecule. C_2 is the twofold symmetry axis. The heavy atom A stays fixed and the hydrogen atoms H_1 and H_2 move transversely to the direction of the bonds so that the angle H_1AH_2 (α) is symmetrically increased by $\delta\alpha$, the $A-H_1$ and $A-H_2$ distances ℓ remaining constant during this process.

"Now the argument there was used for a bond length, but clearly there is no reason why it should not be used for a bond angle." Coulson then went on to consider an illustration of the AH_2 type, of bond length ℓ and angle α (fig. 3). "Suppose we have a molecular-orbital wave function, then we are going to consider how the energy varies as α varies by talking about the *force* The natural thing to do is to suppose that the heavy atom A is kept fixed, as is the length ℓ (fig. 3), and the angle α is just opened out symmetrically, moving the two portions through $\frac{1}{2} \delta\alpha$ each." Then, if δE is the energy involved in changing α to $\alpha + \delta\alpha$,

$$\delta E = -2 F_y \ell \frac{1}{2} \delta\alpha, \tag{9}$$

where the force F_y , embodies both nuclear and electronic contributions. Then, by integration,

$$E = \int_{180^\circ}^{\alpha_v} -\ell F_y d\alpha, \tag{10}$$

where the integration limits go from 180° , taken to be a "zero" for a linear molecule, up to a valence angle of α_v . Coulson concluded: "Now we have got all we really need – we have not got the *absolute* value of energy, but we *have* got an energy variation as the angle changes Now, in order to compare with Walsh's diagrams we have to *reduce* the energy diagrams; and, by a "*reduced*" diagram, I am only going to mean one in which the ordinate has been shifted so that all of the individual energies are zero at 180° (fig. 4)." (In the lecture, Coulson then gave a detailed comparison between the Walsh (fig. 1) and reduced-Walsh diagram, for the details of which the interested

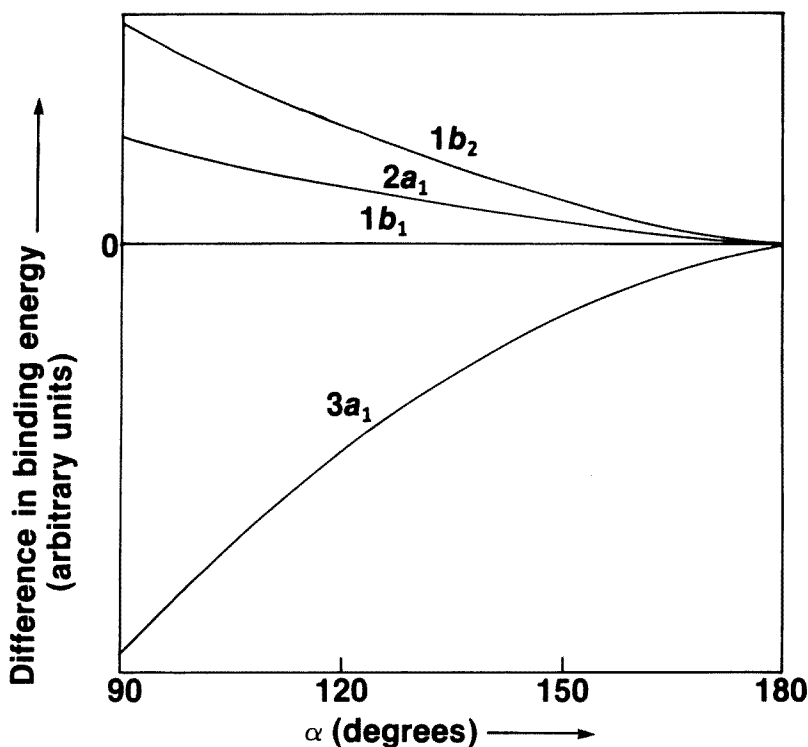


Fig. 4. The "reduced" Walsh diagram for H_2O . (Redrawn, with permission, from ref. [6].)

reader is referred to ref. [6], pp. 418–423.) Coulson also described how the foregoing can be applied to calculate *force constants*, commenting that ". . . whether by good fortune or otherwise – I am not prepared to say – the use of the force method has, in fact, given the most accurate calculation so far made, with respect to force constants, for the particular angular variation we want."

Coulson asked: "What is the chance of any really good calculations by this means? (That is rather giving the game away when I just say it like that!) I think the answer is, really: "not very promising"! When you are using variational methods to get the energy, then you have one enormously favourable feature, and that is that the energy is accurate to one order of magnitude better than the wave function, so that quite reasonably bad wave functions can give you a reasonably good energy. But that does not apply to this kind of discussion; in fact, the error in the force . . . will be of the same order of magnitude as the error in Ψ so that, in general, you would not expect to do as well with this as you would by evaluating energies through some kind of variational process. This could be quite serious with complicated molecules, since most of the approximate wave functions turn out to be really quite constant in the errors that they might lead to."

"Then, secondly, the other Feynman term which is the essential step in this kind of discussion depends upon having either exact wave functions which we know we cannot get, or else Hartree-Fock ones; but in the case of the Hartree-Fock wave function, you are presupposing that only one determinant, or on some occasions quite a number – but only a finite number – normally occurs. You will have no configuration interaction This means that in general – there will be exceptions – ground states may be given better than excited states because, frequently, one gets more configuration interaction in excited states even when there is not very much in ground states. In such a situation, excited states will not be given very well by this method You see, in the course of this discussion, we have been supposing that there is not much configuration interaction. Well – maybe there is!"

"Lastly, something which all of you who are not familiar with it will regard as quite senseless! When we were talking about the AH_2 molecule, I said that the sensible thing to do is to keep atom A fixed and to "swing out" the two hydrogen atoms (fig. 3). But that is not the only way in which I could have distorted the molecule. I could, for example, have kept the *centroid* fixed [fig. 5(a)] Another way

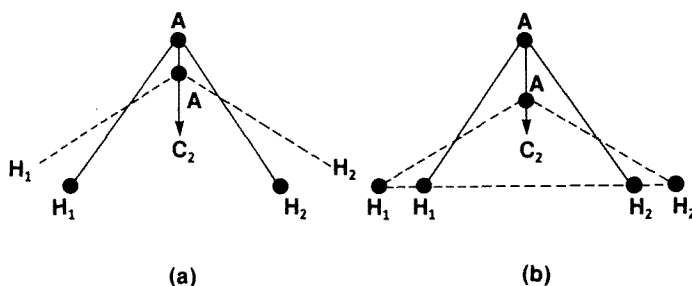


Fig. 5. Symmetric bending of an AH_2 molecule. C_2 is the twofold axis of symmetry. In (a), the centre-of-mass is kept fixed, so that atom A moves along the twofold symmetry axis; in (b), the H atoms (H_1 and H_2) move at right angles to the twofold axis, and the heavy atom A makes an appropriate displacement along the C_1 -axis.

is to let the hydrogens slide on a line [fig. 5(b)] Well, they *are* two alternative ways. Now, obviously they *should* give exactly the same energy – but, when you use wave functions that are not exactly right, you discover, to your horror, that these three approaches give you *different* answers! If I had talked about [fig. 5(a)], we would have obtained a different set of diagrams; if I had talked about [fig. 5(b)], we would have got a different set again – I haven't made slides of them because they don't *look* at all like Walsh diagrams!" [Laughter] (For explanations of these discrepancies, see ref. [6].)

"I think this does rather dampen one's enthusiasm for using this for systems other than ones where hydrogen atoms can be moved; and where you *do* move hydrogen

atoms – for example, in the work on water – you do get a reasonable situation. At any rate, you *are* able to talk about what you are *plotting* in the Walsh diagram – you have got to have something you can *define* in this framework. You also answer the question: should the nuclear term be included? – it should, because there is a force between the nuclei, and also a contribution from the electrons.”

“So we have made *some* progress, even if we have not made as much as we should have liked.”

His friends may well feel that this last statement might serve as a very appropriate epitaph for Professor Coulson.

Acknowledgement

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