

TABLE I. Hyperfine coupling tensors for exchangeable protons. Principal values are given in MHz. Direction cosines are with respect to crystal axes.^{2,3}

		<i>a</i>	<i>b</i>	<i>c</i>
Histidine HCl	100.26	0.320	0.574	0.753
	88.76	0.898	0.066	-0.433
	81.68	-0.298	0.815	-0.495
		<i>a</i> *	<i>b</i>	<i>c</i>
DL Serine	97.32	0.596	0.799	-0.075
	86.22	0.305	-0.139	0.941
	80.66	0.742	-0.584	-0.327
	37.22	0.979	0.171	0.107
	21.16	0.024	-0.629	0.776
	17.86	-0.201	0.758	0.620
	24.48	0.357	0.667	0.652
	10.10	-0.243	0.741	-0.625
	8.72	0.901	-0.064	-0.427

It is of some interest to compare proton couplings in $\dot{\text{C}}-\text{NH}_2$ and $\dot{\text{C}}-\text{OH}$ radicals. Information concerning the latter radicals, which are also substantially planar,⁶ is meager. The few available data are included in

Fig. 1. Evidently the anisotropy of the coupling of protons in the latter radicals is significantly more than in the former which is to be expected since the carbon-hydrogen distance is larger in $\dot{\text{C}}-\text{NH}_2$ radicals by a factor of 1.06.⁷ The anisotropy arises from dipole-dipole coupling which varies approximately as the inverse cube of this distance.

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COMMENTS

On approximate energy differences from average electron densities

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Density functional theory is presently an active area of research because the dimensionality of the electron density is far less than that of the many-electron wavefunction. Since the universal density functional¹ is presently unknown, knowledge of equations which relate eigenstate densities to their corresponding energies is important because fulfillment of these equations constitute necessary eigenstate conditions. In other words, for a trial functional to be correct, it would have to generate densities and corresponding energies which satisfy these conditions.

One approximate equation, which involves an average electron density was recently put forth for atoms.² A purpose of the present Comment is to point out that the equation is a special case of a more general equation which is applicable to molecules as well as to atoms.

Consider isoelectronic systems *A* and *B*, with Hamiltonians \hat{H}_A and \hat{H}_B , which differ in external potentials. For example, \hat{H}_A and \hat{H}_B might differ in nuclear charges or in internuclear distances. If Ψ_A and Ψ_B are ground eigenstates, then by the variational theorem:

$$E_B < \langle \Psi_A | \hat{H}_A + \Delta \hat{H} | \Psi_A \rangle, \quad (1)$$

and

$$E_A < \langle \Psi_B | \hat{H}_B - \Delta \hat{H} | \Psi_B \rangle, \quad (2)$$

or

$$E_B = E_A + \int d\mathbf{r} \Delta \hat{v}(\mathbf{r}) \rho_A^{(r)} - \delta_A; \delta_A > 0, \quad (3)$$

and

$$E_A = E_B - \int d\mathbf{r} \Delta \hat{v}(\mathbf{r}) \rho_B^{(r)} - \delta_B; \delta_B > 0, \quad (4)$$

where, for instance, $\hat{v}(\mathbf{r}) = -\sum_{\alpha} Z_{\alpha} / |\mathbf{R}_{\alpha} - \mathbf{r}|$.

Subtraction of Eq. (4) from Eq. (3) yields the desired general expression. Namely,

$$E_B - E_A = \int d\mathbf{r} \Delta \hat{v}(\mathbf{r}) \rho_{av}^{(r)} + \Delta, \quad (5)$$

where

$$\rho_{av} = \frac{1}{2}(\rho_A + \rho_B), \quad (6)$$

TABLE I. Comparison of ground-state energy differences obtained from average electron densities with those obtained from the truncated perturbation expansion.^a

Process	From truncated expansion ^b	From average density ^{c,d}	Exact ^e
He → H ⁺	2.37500	2.37158	2.37597
Li ⁺ → He	4.37500	4.37624	4.37619
B ³⁺ → Be ²⁺	8.37500	8.37541	8.37541
N ⁵⁺ → C ⁴⁺	12.37500	12.37520	12.37520
F ⁷⁺ → O ⁶⁺	16.37500	16.37512	16.37512
Na ⁹⁺ → Ne ⁸⁺	20.37500	20.37508	20.37508

^aEnergy differences are given in atomic units.

^bComputed with Eq. (10), where $\epsilon_0 = -1$ and $\epsilon_1 = 5/8$.

^cComputed with Eq. (5).

^dThe integrals were obtained from the recent accurate calculations reported in A. J. Thakkar and V. H. Smith, Phys. Rev. A 15, 1 (1977).

^eThese are the exact energy differences through 5 decimal places. See, for instance, the reference in footnote d.

and where

$$\Delta = \frac{1}{2}(\delta_B - \delta_A) . \quad (7)$$

Further, addition of Eqs. (3) and (4) gives a bound to $|\Delta|$. Namely

$$|\Delta| < \frac{1}{2} \int d\mathbf{r} \Delta \hat{v}(\mathbf{r}) [\rho_A^{(r)} - \rho_B^{(r)}] . \quad (8)$$

There will be situations where the error term Δ will be identically zero since δ_A and δ_B are always *both positive*. For example, in atoms, $|\Delta|$ approaches zero in the limit of infinite nuclear charges. In any case, it is expected that $|\Delta|$ should decrease rapidly as $\hat{H}_B \rightarrow \hat{H}_A$, for molecules as well as for atoms.

It was demonstrated empirically² that $|\Delta|$ is generally quite small for adjacent members of an atomic isoelectronic sequence. One rationalization was provided² by combining³ the Hellmann–Feynman theorem with the following perturbation expansion in powers of the nuclear

charge Z :

$$E(Z) = \sum_{n=0}^{\infty} \epsilon_n Z^{(2-n)} . \quad (9)$$

It was shown² that $\Delta = 0$ if

$$E(Z) = \epsilon_0 Z^2 + \epsilon_1 Z + \epsilon_2 . \quad (10)$$

Thus, if all $\epsilon_n = 0$, for $n > 2$, then exact energy differences would be given by column 2 in Table I, and columns 2 and 4 would be identical. While column 2 does, in fact, give accurate values, the values in column 3 are significantly more accurate (except for the change He → H⁺). Therefore, even though the contributions to $E_B - E_A$ by the ϵ_n , for $n > 2$, are not negligible, $\int d\mathbf{r} \Delta \hat{v}(\mathbf{r}) \rho_{av}^{(r)}$ very adequately accommodates these higher order contributions. By straightforward algebraic manipulations utilizing Eq. (9) and the Hellmann–Feynman relation, the expression for Δ , when $Z_B - Z_A = 1$, is found to be given by

$$\Delta = - \left(\frac{0.5}{Z_A^4 + 2Z_A^3 + Z_A^2} \right) \epsilon_3 + \left(\frac{2Z_A + 1}{Z_A^6 + 3Z_A^5 + 3Z_A^4 + Z_A^3} \right) \epsilon_4 + \dots \quad (11)$$

The above expression reveals that $|\Delta|$ is extremely small, even at moderately low Z_A , because the denominators contain Z_A raised to high powers as early as the ϵ_3 term.

In closing, it is important to note that the average electron density approximates the transition density in the integral Hellmann–Feynman formula⁴ which is an exact expression for isoelectronic changes. This approximation was utilized and analyzed by Wyatt and Parr in their studies of the barrier to rotation in ethane.⁵

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