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Description of diatomic molecules using one electron configuration energies with two-body interactions

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It has recently been shown that the vibrational potential energy for a diatomic molecule α–β may be written exactly in the form (i) $W(R) = W_\beta(R) + W_{NPF}(R)$, where $W_\beta(R)$ is the electrostatic interaction energy between nucleus α and the free atom β and $W_{NPF}(R)$ is the electrostatic interaction energy between nucleus α and the "Non-Perfectly-Following" electronic charge density redistributions arising when atoms α and β form the molecule α–β with the internuclear distance R. In this paper it is shown that $W_{NPF}(R)$ may be approximated, within a constant near equilibrium, by the extended Hückel configurarion energy, taken as a simple sum of orbital energies, $W_{EH}(R)$, yielding an approximate molecular energy $W^*(R)$ according to the formula (ii) $W^*(R) = W_\beta + W_{EH}(R)$. Comparisons are made between $W^*(R)$ and the experimental $W(R)$ for first and second period diatomic molecules. Equation (ii) overcomes the deficiency present when either $W_\beta(R)$ or $W_{EH}(R)$ alone is used to estimate equilibrium internuclear distances, although equilibrium force constants may be derived from $W_\beta(R)$ if the equilibrium distances are known.

The extended Hückel method[1] is the simplest all-valence-electron semiempirical molecular orbital method. It is basically a one-electron theory, with the energy being taken as a simple sum of one-electron energy levels. While the extended Hückel theory provides a good initial approximation to the electronic structure of complex molecules, and has been extremely useful in advancing our understanding of molecules, the method has some obvious deficiencies. Though the energies of angular deformations in molecules are well represented, the theory does not yield good potential energy curves for stretching motions. It is likely that two-body electrostatic interactions are not well simulated by the extended Hückel method. In this paper we attempt to remedy this deficiency by adding to the extended Hückel configuration energy some pairwise interaction energies. Good equilibrium internuclear distances and vibrational potential functions result from this procedure. Results for first and second period diatomic molecules are displayed.

METHOD

Molecular orbitals and their energies are determined with the extended Hückel procedure.[1] The molecular orbital wavefunctions ψ take the form

$$\psi = \sum_\gamma c_\gamma \varphi_\gamma , \tag{1}$$

where γ spans all the Slater-type atomic orbitals in the basis set of valence orbitals and the c_γ are chosen to diagonalize the Hamiltonian matrix. Off-diagonal Hamiltonian matrix elements $H_{\alpha\beta}$ are approximated by the Wolfsberg–Helmholz formula

$$H_{\alpha\beta} = (K/2)(H_{\alpha\alpha} + H_{\beta\beta}) S_{\alpha\beta} , \tag{2}$$

where K is a constant, $H_{\alpha\alpha}$ and $H_{\beta\beta}$ are valence state ionization energies for atomic orbitals on atom α and atom β, and $S_{\alpha\beta}$ is the overlap integral for φ_α and φ_β. The total or configuration energy is the sum of the occupied molecular orbital energies and is written $W_{EH}(R)$, where R is the distance between nucleus α and nucleus β.

To derive the two-body electrostatic interaction energy, the exact electronic charge density $\rho(R_\alpha, \mathbf{r})$ for a diatomic molecule $\alpha - \beta$ is written[2]

$$\rho(R_\alpha, \mathbf{r}) = \rho_\beta(\mathbf{r}) + \rho_\alpha(R_\alpha - \mathbf{r}) + \rho_{NPF}(R_\alpha, \mathbf{r}) , \tag{3}$$

where the origin of the coordinate system is on nucleus β. $\rho_\beta(\mathbf{r})$ and $\rho_\alpha(R_\alpha - \mathbf{r})$ are atomic charge densities centered on nucleus β and nucleus α. These densities are computed using the same Slater exponents as those in the extended Hückel calculation. $\rho_{NPF}(R_\alpha, \mathbf{r})$ is the "Non-Perfectly-Following" correction to the atomic electronic charge densities which makes Eq. (3) exact. By integrating the Hellmann–Feynman formula for the force on nucleus α, the exact energy $W(R_\alpha)$ of the molecule is found to be given by the formula[3]

$$W(R_\alpha) = W_\beta(R_\alpha) + W_{NPF}(R_\alpha) , \tag{4}$$

where

$$W_\beta(R_\alpha) = Z_\alpha [Z_\beta R_\alpha^{-1} - \int \rho_\beta(\mathbf{r}) |R_\alpha - \mathbf{r}|^{-1} d\mathbf{r}] \tag{5}$$

$$W_{NPF}(R_\alpha) = -Z_\alpha \int_{-\infty}^{R_\alpha} \int \rho_{NPF}(R'_\alpha, \mathbf{r}) \frac{d}{dR'_\alpha} |R'_\alpha - \mathbf{r}|^{-1} d\mathbf{r}\, dR'_\alpha . \tag{6}$$

In these equations $W_\beta(R_\alpha)$ is the electrostatic energy for the interaction of nucleus α with neutral atom β and is repulsive, and $W_{NPF}(R_\alpha)$ is the energy due to electronic charge density redistributions taking place as the atoms come together to form the molecule. The Appendix gives explicit expressions for $W_\beta(R)$.

The Laplacian of Eq. (4) yields a Poisson equation.[2] For diatomic molecules the angular terms vanish, leaving the radial equation

$$k_e = \nabla^2_{R_\alpha} W(R_\alpha) = \nabla^2_{R_\alpha} W_\beta(R_\alpha) = 4\pi Z_\alpha \rho_\beta(R_\alpha) \tag{7}$$

which, when evaluated at the equilibrium internuclear distance, yields estimates of k_e, the quadratic force constant. Because Eq. (7) gives good predictions of k_e, $\nabla^2_{R_\alpha} W_{NPF}(R_\alpha)$ must be approximately zero near equilib-

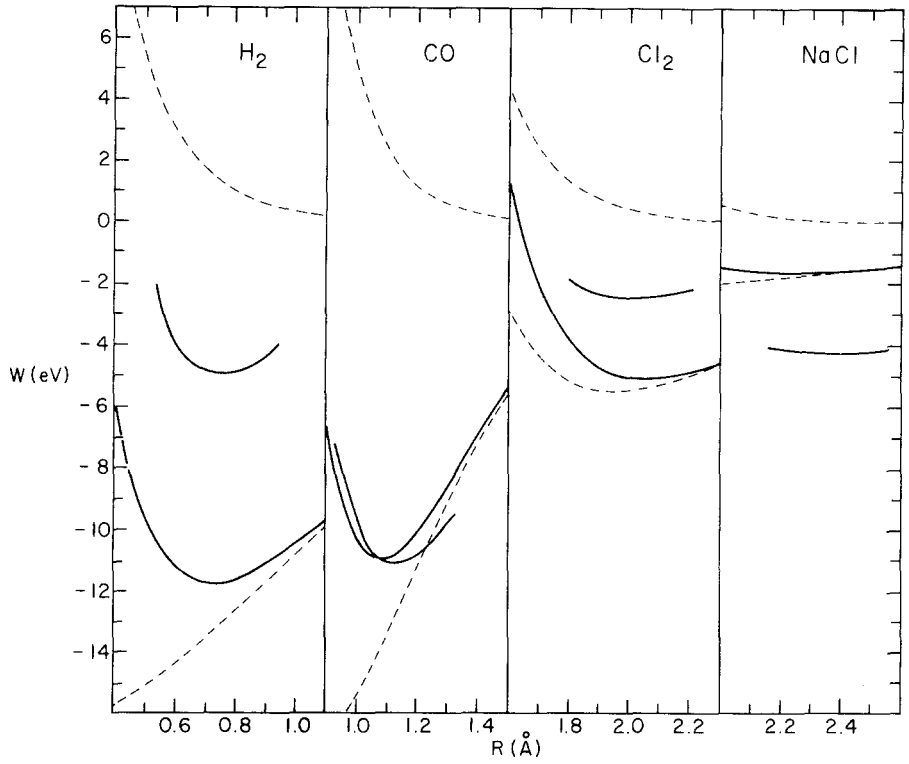

FIG. 1. The two-body energy $W_\beta(R)$ is the dashed repulsive line; $W_{EH}(R)$ the dashed attractive line. The calculation energy $W^*(R)$ is the long heavy line; the experimental energy $W(R)$ is the short heavy line. $W(R)$ was calculated as in Ref. 4.

rium, implying $W_{NPF}(R_\alpha)$ is attractive and of the form[3]

$$W_{NPF}(R_\alpha) \propto R_\alpha^{-1} \tag{8}$$

near equilibrium in the limiting case that Eq. (7) is exact. Implications and applications of the theory to diatomic and larger molecules are in Ref. 3.

The energy $W_{NPF}(R_\alpha)$ corresponds to the binding energy component of $W(R)$ and is identified with $W_{EH}(R_\alpha)$. The subscript α is dropped and the approximate total molecular energy $W^*(R)$ is written

$$W^*(R) = W_\beta(R) + W_{EH}(R) \quad . \tag{9}$$

Equation (9) is the formula tested in this paper.

RESULTS AND DISCUSSION

The repulsive and attractive energy components $W_\beta(R)$, W_{EH}, the calculated total energy $W^*(R)$, and the experimental[4] $W(R)$ are plotted in Fig. 1 for four disparate di-

TABLE I. Comparison of bond lengths estimated from Eq. (9) with experiment.

Molecule	Bond lengths (Å) Estimated	Experimental[a]
H_2	0.73	0.74
Li_2	2.73	2.67
C_2	1.24	1.24
N_2	1.17	1.09
F_2	1.45	1.41
P_2	1.89	1.89
Cl_2	2.04	2.00
CH	1.15	1.12
LiF	1.32	1.54
BF	1.12	1.27
CO	1.09	1.13
PN	1.61	1.49
FCl	1.76	1.63
BCl	1.54	1.72
SiS	1.87	1.93
CS	1.58	1.53
SiO	1.59	1.51
NaCl	2.28	2.36
AlCl	1.85	2.14

[a]Taken from Ref. 4 of the text. All examples are $^1\Sigma$ states except CH which is $^2\Pi$.

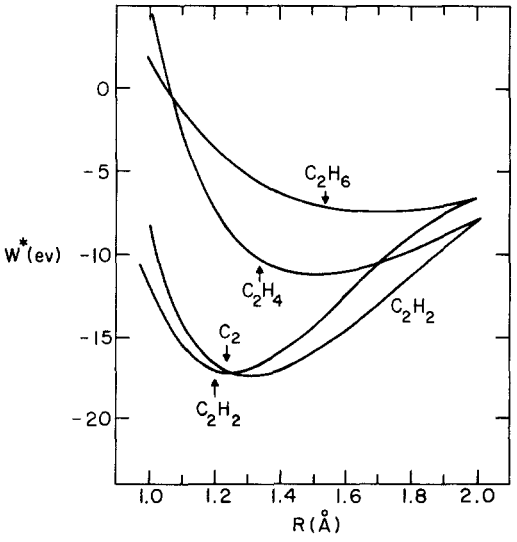

FIG. 2. Calculated total energies $W^*(R)$ for C_2, acetylene, ethylene, and ethane. CH bond lengths were fixed at 1.09 Å. R is the CC distance, arrows marking the correct equilibrium values.

atomics: H_2, Cl_2, CO, and NaCl. Table I compares calculated and experimental bond lengths for a larger set of molecules. In each case $W_\beta(R)$ is calculated using the density of the more electronegative atom. In extended Hückel calculations a value of 1.75 for the Wolfsberg–Helmholz constant K in Eq. (2) is typically used. For the purpose of these calculations we have found that a K value of 2.25 gives better agreement with experiment, and this value has been used throughout. The basis sets excluded $3d$ orbitals on second row atoms.

It is evident that equilibrium distances and force constants are well determined by Eq. (9). The range of usefulness of Eq. (9) is clear from the variety of molecules considered. In all cases $W_\beta(R)$ is repulsive and $W_{EH}(R)$ is attractive. For F_2, Cl_2, and FCl there is a repulsive component in $W_{EH}(R)$ at distances smaller than the equilibrium separation.

The homonuclear $W^*(R)$ curves lie below the experimental $W(R)$ ones but their shapes are good. All calculated equilibrium internuclear distances are within 0.08 Å of the experimental ones. For the covalent heteronuclear molecules some $W^*(R)$ are above $W(R)$ and some below. Predicted equilibrium distances are within 0.13 Å of the experimental ones.

For the more highly ionic heteronuclear molecules LiF, NaCl, BF, SiO, and AlCl $W^*(R)$ curves lie above the experimental ones, probably because ionic contributions to the energies are omitted. It is not clear what form such contributions should take; however, squaring the calculated atomic charges and dividing by R yields a nearly constant contribution near equilibrium which improves the binding energy. The extended Hückel method frequently overestimates atomic charges, so additional ionic contributions are not yet a suggested calculational modification to Eq. (9). Predicted equilibrium distances are around 0.2 Å too small.

Figure 2 shows results for $^1\Sigma_g^+$ C_2, acetylene, ethylene, and ethane for which estimates of CC equilibrium distances are 0.00, 0.10, 0.15, and 0.15 Å too large. This implies the antibonding character in the molecular orbitals prevents $W_{EH}(R)$ from decreasing rapidly enough as R decreases. Multiplying Eq. (2) by a constant times an exponential function in R might correct this and might also raise the homonuclear $W^*(R)$ curves.

The extension of Eq. (9) to polyatomic molecules and clusters is obvious.[3] What must be done is to replace $W_\beta(R)$ with all appropriate two-body interaction energy terms. Some modification of Eq. (2) may be necessary. The advantage of such an approach would be the retention of the economy of the extended Hückel description while at the same time obtaining energy surfaces of improved accuracy.

ACKNOWLEDGMENT

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APPENDIX

For a period 1 atom Eq. (5) of the text takes the form

$$W_\beta(R) = Z_\alpha N \frac{\zeta^3}{4!}\left(R^2 + \frac{6R}{\zeta} + \frac{18}{\zeta^2} + \frac{24}{\zeta^3 R}\right)\exp(-\zeta R) \quad , \qquad \text{(A1)}$$

where N is the number of L-shell electrons and ζ is twice the Slater exponent of the $2s$ and $2p$ functions for atom β. Similarly, for a period 2 atom, it takes the form

$$W_\beta(R) = Z_\alpha N \frac{\zeta^5}{6!} \times \left(R^4 + \frac{10R^3}{\zeta} + \frac{60R^2}{\zeta^2} + \frac{240R}{\zeta^3} + \frac{600}{\zeta^4} + \frac{720}{\zeta^5 R}\right)\exp(-\zeta R). \qquad \text{(A2)}$$

[1] R. Hoffmann, J. Chem. Phys. **39**, 1397 (1963); R. Hoffmann and W. N. Lipscomb, *ibid.* **36**, 2179 (1962); **37**, 2872 (1962). First row Slater exponents and $2s$ and $2p$ valence state ionization energies and second row Slater exponents and $3s$ and $3p$ valence state ionization energies in eV used in this paper are as follows: Li—0.65, 5.4, 3.5; B—1.3, 15.2, 8.5; C—1.625, 21.4, 11.4; N—1.95, 26.0, 13.4; O—2.275, 32.3, 14.8; F—2.425, 40.0, 18.1; Na—0.733, 5.1, 3.0; Al—1.167, 12.3, 6.5; Si—1.383, 17.3, 9.2; P—1.6, 18.6, 14.0; S—1.817, 20.0, 13.3; Cl—2.033, 30.0, 15.0. For H the $1s$ Slater exponent of 1.3 and valence state ionization energy of 13.6 are used.

[2] A. B. Anderson and R. G. Parr, J. Chem. Phys. **53**, 3375 (1970).

[3] A. B. Anderson, J. Chem. Phys. **60**, 2477 (1974).

[4] For all the diatomic examples the experimental $W(R)$ curve is determined by adding to the energy of binding [A. G. Gaydon, *Dissociation Energies* (Chapman and Hall Ltd., London, 1953)] terms calculated from the 4th order Taylor series expansion of the vibrational potential energy [D. R. Herschbach and V. W. Laurie, University of California Radiation Laboratory Report No. UCRL9694, Berkeley, CA, 1961 (unpublished)].