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ARTICLES

Molecular Geometries by the Extended Hückel Molecular Orbital Method

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Bond length calculations with the extended Hückel molecular orbital (EHMO) approximation can be improved by adding a two-body repulsive energy term and a distance-dependent Wolfsberg–Helmholz constant $K = k \exp(-\delta R)$. As demonstrated in the case of simple homonuclear two-level interactions, such a distance-dependent K leads to problems, however. This drawback of the otherwise very useful improvement of the EHMO method can be overcome by applying $K = 1 + \kappa \exp(-\delta(R - d_0))$. d_0 is equal to the sum of the orbital radii of the two adjacent atoms, and κ is calculated from the weighted Wolfsberg–Helmholz formula. The new formula leads to good potential energy curves for diatomic and for polyatomic molecules.

1. Introduction

The extended Hückel molecular orbital (EHMO) theory provides a good initial approximation to the electronic structure of complex molecules. It is the simplest of the all valence one-electron theories and is very useful for advancing our understanding of molecules, complexes, semiconductors, and other systems. The search for the stationary points of energy hypersurfaces, especially for their local minima and saddle points, is of fundamental significance for studies of chemical reactivity. The EHMO method in its original form has been successfully applied to describe pathways in important organic and inorganic reactions.[1-6] Problems arising from overestimating "counterintuitive orbital mixing" have been discussed and solved by introducing the so-called weighted Wolfsberg–Helmholz formula.[7] Despite this, the EHMO method in its original form does not correctly include electrostatic interaction and therefore fails in many cases to yield good potential energy curves for stretching modes. Anderson and Hoffmann[8] have shown how this deficiency can be overcome by adding two-body electrostatic correction terms, applying the Hellmann–Feynman theorem. To derive the two-body electrostatic interaction energy, the exact electronic charge density $\rho(R_\alpha,r)$ for a diatomic molecule α–β is written as

$$\rho(R_\alpha,r) = \rho_\beta(r) + \rho_\alpha(R_\alpha - r) + \rho_{\mathrm{NPF}}(R_\alpha,r) \qquad (1)$$

where the origin of the coordinate system is on nucleus β. $\rho_\beta(r)$ and $\rho_\alpha(R_\alpha - r)$ are atomic charge densities, centered on nucleus β and nucleus α. These densities are computed by using the same Slater orbitals as those in the extended Hückel calculation. $\rho_{\mathrm{NPF}}(R_\alpha,r)$ is the "non-perfectly-following" correction to the atomic charge densities which makes eq 1 exact. The energy $E(R)$ is expressed as sum of the electrostatic two-body correction $E_{\alpha\beta}(R)$ and the extended Hückel binding energy $\Delta E_{\mathrm{EHMO}}(R)$:

$$E(R) = E_{\alpha\beta}(R) + \Delta E_{\mathrm{EHMO}}(R) \qquad (2)$$

The extended Hückel binding energy is calculated according to[9]

$$\Delta E_{\mathrm{EHMO}}(R) = E_{\mathrm{EHMO}}(R) - \sum_\mu b_\mu E_\mu^\circ \qquad (3)$$

where $\sum b_\mu E_\mu^\circ$ is the sum of the atomic valence orbital ionization potentials, each of them times the orbital occupation number b_μ.

In a short article,[10] Anderson discussed the basis of the EHMO method with corrections and tried to improve calculations of dissociation energies by multiplying the Wolfsberg–Helmholz constant with $\exp(-\delta R)$:

$$H_{ij} = \tfrac{1}{2}K(H_{ii} + H_{jj})S_{ij} \qquad (4a)$$

$$K = k \exp(-\delta R); \quad k = 2.25,\ \delta = 0.13\ \text{Å}^{-1} \qquad (4b)$$

In later applications of this approach, he obtained good results on many different systems.[11-15]

2. Criticism

Despite these interesting results, formula 4b leads to problems, because K becomes smaller than 1 for large bond distances. These problems do not affect the results in the neighborhood of the energy minimum, but they lead to wrong behavior at medium and large bond distances. This is an unnecessary burden to the otherwise useful method. We shall therefore show how formula 4b can be corrected by fully maintaining the advantages of a distance-dependent K.

Let us first explain why the condition $K > 1$ for $R < \infty$ should always be fulfilled. H_2^+ is the simplest one-electron system that can be treated very accurately within the LCAO–MO approach. The results are

$$\Psi_\mp = \frac{1}{[2(1 \mp S)]^{1/2}}(1s_A \mp 1s_B); \quad E_\mp = \frac{H_{AA} \mp H_{AB}}{1 \mp S} + \frac{1}{R}$$

$$H_{AA} = E_H(\zeta) + \left\langle 1s_A \middle| -\frac{1}{r_B} \middle| 1s_A \right\rangle; \quad S = \langle 1s_A | 1s_B \rangle$$

$$H_{AB} = E_H(\zeta)S + \left\langle 1s_A \middle| -\frac{1}{r_A} \middle| 1s_B \right\rangle; \quad E_H(\zeta) = -\frac{\zeta^2}{2} \qquad (5)$$

ζ is used as a variational parameter which takes the values $\zeta =$

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2 at $R = 0$, $\zeta = 1.228$ at $R = R_0$, and $\zeta = 1$ at $R \to \infty$. Bond length and bond energy calculated with this approach differ by less than 1% from the experimental values.

Let us examine the energy difference between the bonding and the antibonding orbital:

$$E_+ - E_- = \frac{2}{1 - S^2}(H_{AB} - H_{AA}S) \tag{6}$$

Since H_{AA} and H_{AB} are both negative and S is positive, the condition $H_{AB} < H_{AA}S$ must hold to avoid crossing of E_+ and E_-. In the case of H_2^+ this is fulfilled.

More generally, a two-level interaction X–X with $H_{AB} = H_{BA}$ can be described as

$$\begin{vmatrix} H_{AA} - \epsilon & H_{AB} - \epsilon S \\ H_{AB} - \epsilon S & H_{AA} - \epsilon \end{vmatrix} = 0$$

from which we get

$$\epsilon_+ = \frac{H_{AA} + H_{AB}}{1 + S}; \quad \epsilon_- = \frac{H_{AA} - H_{AB}}{1 - S}$$

and therefore

$$\Delta E_+ = \epsilon_+ - H_{AA} = \frac{H_{AB} - SH_{AA}}{1 + S}$$

$$\Delta E_- = \epsilon_- - H_{AA} = -\frac{H_{AB} - SH_{AA}}{1 - S} \tag{7}$$

Dividing ΔE_+ by ΔE_- leads to

$$\frac{\Delta E_+}{\Delta E_-} = -\frac{1 - S}{1 + S} < 0, \quad \text{for } 0 < S < 1$$

This means that in the interval $0 < S < 1$ ΔE_+ and ΔE_- never do change their sign. If X–X forms a chemical bond, ϵ_+ describes the bonding interaction and ϵ_- the antibonding interaction in the neighborhood of the equilibrium bond distance. As a consequence, $\epsilon_+ < \epsilon_-$ and therefore $\Delta E_+ < \Delta E_-$. From this follows that ΔE_+ and ΔE_-, and therefore ϵ_+ and ϵ_-, will never cross in such a two-level interaction. In our opinion any semiempirical parametrization should take this aspect into account.

If we now approximate the off-diagonal elements H_{AB} by means of eq 4a, we get

$$H_{AB} = KH_{AA}S \tag{8}$$

Inserting (8) into (7) leads to

$$\Delta E_+ = H_{AA}(K - 1)\frac{S}{1 + S}; \quad \Delta E_- = -H_{AA}(K - 1)\frac{S}{1 - S} \tag{9}$$

We conclude that ΔE_+ and ΔE_-, and therefore ϵ_+ and ϵ_-, do not cross, as long as K is larger than 1. One of the basic rules of the MO theory is the following:[7]

"Constructive interference of AOs leads to bonding MOs exhibiting one-electron energies lowered relative to the weighted average of the diagonal elements H_{ii} of the contributing AOs, while destructive interference leads to antibonding MOs exhibiting one-electron energies raised relative to the corresponding average of H_{ii}'s." If we allow K to become smaller than 1, this rule is obviously violated.

We now estimate the dissociation energy D_e of homonuclear diatomic molecules that, to a first approximation, can be described by 9, i.e., by a $(ns\sigma_g)^2$ electron configuration. Such molecules are H_2, Li_2, ..., Cs_2, Cu_2, Ag_2, Au_2.

Within the extended Hückel approach, D_e should be approximately equal to $-2\Delta E_+$:[16-18]

$$D_e \approx -2H_{AA}(K - 1)\frac{S}{1 + S} \tag{10}$$

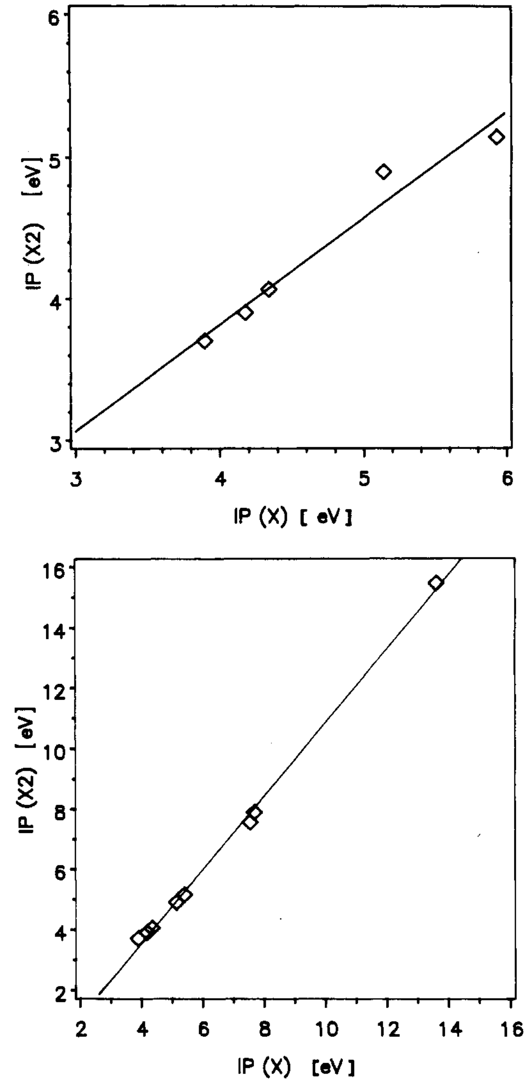
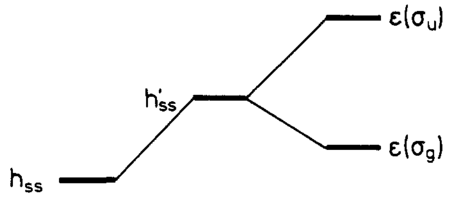


Figure 1. Adiabatic ionization potentials of homonuclear dimers versus ionization potentials of the $(ns)^1$ electron of the atoms: (top) Li_2 to Cs_2; (bottom) H_2, Li_2, ..., Cs_2, Cu_2, and Ag_2.

SCHEME I



If $K < 1$, D_e would become negative which corresponds to a nonphysical situation. Similar arguments hold for the energy of the first electronic transition $\sigma_u \leftarrow \sigma_g$ and for the first adiabatic ionization energy of these molecules.[16,18] It is interesting to note that, from the expression for ϵ_+ and eq 8, one would expect a linear relationship to hold approximately because the $\langle ns_x|ns_{x'}\rangle$ overlap integral in these homonuclears is very similar:

$$\text{IP}[X_2(i)] = a_0 + a_1\text{IP}[X_i] \tag{11}$$

with $a_1 = (1 + KS)/(1 + S)$ and with a_0 reflecting the electron–electron interaction, not included in the one-electron orbital energy ϵ_+. This means that the ionization potential of the dimers is proportional to the ionization potential of the atoms plus a constant.

In Figure 1 we show that this prediction is correct for the alkali-metal dimers and that it is also a good approximation for

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TABLE I: Comparison of Experimental and Calculated Data of Some Diatomic and Polyatomic Molecules[a]

a. Diatomic Molecules

molecule	r_e	IP_1	A ← X	ΔE	D_0[a]
H_2	0.74	15.43	$^1\Sigma_u{}^+ \leftarrow {}^1\Sigma_g{}^+$	11.37	4.48
	0.80	15.37	$\sigma_g\sigma_u \leftarrow \sigma_g^2$	16.74	5.52
Li_2	2.67	5.0	$^1\Sigma_u{}^+ \leftarrow {}^1\Sigma_g{}^+$	1.74	1.05
	2.31	5.22	$\sigma_g\sigma_u \leftarrow \sigma_g^2$	2.88	2.18
Ag_2	2.48	7.56	$^1\Sigma_u{}^+ \leftarrow {}^1\Sigma_g{}^+$	2.85	1.66
	2.81	7.82	$\sigma_g\sigma_u \leftarrow \sigma_g^2$	1.55	3.15
C_2	1.24	12.15	$c \leftarrow {}^1\Sigma_g{}^+$		6.21
	1.28	12.11	$\pi_u^3\sigma_g^1 \leftarrow \pi_u^4$	2.17	5.83
LiH	1.60	7.7	$^1\Sigma^+ \leftarrow {}^1\Sigma^+$	3.28	2.43
	1.63	9.50	$\sigma^1\sigma^1 \leftarrow \sigma^2$	3.17	2.66
CuH	1.46		$^1\Sigma^+ \leftarrow {}^1\Sigma^+$	2.91	2.7
	1.38	11.23	$\sigma^1\sigma^1 \leftarrow \sigma^2$	4.32	3.91
AgH	1.62		$^1\Sigma^+ \leftarrow {}^1\Sigma^+$	3.71	2.28
	1.71	11.26	$\sigma^1\sigma^1 \leftarrow \sigma^2$	3.42	3.74
HCl	1.27	12.75	$c \leftarrow {}^1\Sigma^+$		4.43
	1.42	12.86	$\pi^1\sigma^1 \leftarrow \pi^2$	10.98	4.07
CO	1.13	14.01	$c \leftarrow {}^1\Sigma^+$		11.09
	1.35	13.35	$\sigma^1\pi^1 \leftarrow \sigma^2$	2.74	5.10
CS	1.53	11.33	$c \leftarrow {}^1\Sigma^+$		7.35
	1.59	11.11	$\sigma^1\pi^1 \leftarrow \sigma^2$	2.65	5.36
SiO	1.51	11.40	$c \leftarrow {}^1\Sigma^+$		8.26
	2.20	11.10	$\pi^3\pi^1 \leftarrow \pi^4$	0.93	1.38

b. Polyatomic Molecules

molecule	r_e	Φ_e	IP	HOMO	LUMO
H_2O	0.96	105.2	12.61		
	1.15	111.5	12.81	nb_1	σ^*b_2
H_2S	1.33	92.2	10.47		
	1.39	103.0	11.46	nb_1	σ^*b_2
CO_2	1.16	*d*	13.77		
	1.40	*d*	13.74	$\pi\pi_g$	$\pi^*\pi_u$
CH_2O	1.21, 1.10	121.1	10.88		
	1.43, 1.18	124.0	11.88	nb_2	π^*b_1
CH_4	1.09	*e*	12.99		
	1.15	*e*	13.74	σt_2	σ^*t_2
SiH_4	1.48	*e*	12.82		
	1.58	*e*	14.10	σt_2	σ^*t_2

[a] For each molecule, the upper and lower numbers represent experimental and calculated data, respectively. Distances are in angstroms and energies in electronvolts. $1 + \kappa = 1.75$, $\delta = 0.13$. [b] D_0(calcd) = D_e(calcd) − $1/2\omega_e$. [c] Not directly comparable symmetry states. [d] Linear. [e] Tetrahedral.

TABLE II: Comparison of Experimental and Calculated Data for Molecules with C–O Multiple Bonds[a]

molecule	r_e	IP	A ← X	ΔE	D_0[a]
CO	1.13	14.01	$c \leftarrow {}^1\Sigma^+$		11.09
	1.15	13.18	$\sigma^1\pi^1 \leftarrow \sigma^2$	4.75	9.43
SiO	1.51	11.43	$c \leftarrow {}^1\Sigma^+$		8.26
	1.55	11.73	$\sigma^1\pi^1 \leftarrow \sigma^2$	3.7	8.20

molecule	r_e	Φ_e	IP	HOMO	LUMO
CO_2	1.16	*d*	14.01		
	1.20	*d*	13.66	$\pi\pi_g$	$\pi^*\pi_u$
CH_2O	1.21, 1.10	121.1	12.18		
	1.23, 1.08	119.0	11.88	nb_2	π^*b_1

[a] For each molecule, the upper and lower numbers represent experimental and calculated data, respectively. Distances are in angstroms and energies in electronvolts. $1 + \kappa = 2.00$, $\delta = 0.35$, and $1 + \kappa = 2.25$ for SiO. [b] D_0(calcd) = D_e(calcd) − $1/2\omega_e$. [c] Not directly comparable symmetry states. [d] Linear.

the series H_2 to Ag_2. From this data we extrapolate IP[Au_2] = 9.18 eV which has not yet been measured, as far as we know. The experimental values have been taken from ref 19–21.

Equation 11 supports the general validity of Scheme I for the description of the $(ns\sigma_g, ns\sigma_u)$ levels and of the $B^1\Sigma_u{}^+ \leftarrow X^1\Sigma_g{}^+$ transitions of H_2 to Au_2.[16-18] h_{ss} is the atomic valence orbital ionization potential, and h_{ss}' is the valence orbital ionization potential after the atoms have approached bond distance.

The aim of this section is to emphasize that the above given interference rule should not be violated in a one-electron scheme for the description of chemical bonds, unless very special conditions apply as discussed in ref 7. Consequently, $K > 1$ must be fulfilled for finite bond distances.

3. Correction

We now give a correction that maintains all the advantages of a distance-dependent K but circumvents the mentioned problems of eq 4b. We propose the following equation:

$$K = 1 + \kappa \exp[-\delta(R - d_0)] \qquad (12a)$$

κ and δ are positive empirical parameters while d_0 is equal to the sum of the orbital radii $r_n(A) + r_n(B)$ which are defined by the following equation:

$$r_n = \frac{1}{\int_0^\infty (1/r) R_{nl}{}^2(r) r^2 \, dr} \qquad (13)$$

For Slater-type orbitals this leads to (14a) and in case of double-ζ functions to (14b):

$$r_n = (n/\zeta) a_0 \qquad (14a)$$

$$r_n = \frac{n}{c_1{}^2\zeta_1 + c_2{}^2\zeta_2 + \dfrac{2^{2n}(\zeta_1\zeta_2)^{n+1/2}}{(\zeta_1 + \zeta_2)^{2n}}} a_0 \qquad (14b)$$

a_0 is the Bohr radius, and d_0 corresponds approximately to observed bond distances. This means that in the neighborhood of the equilibrium bond distance, eq 12a takes the simple form

$$K(R = d_0) = 1 + \kappa \qquad (12b)$$

Instead of introducing a new parameter κ, this allows to calculate κ by means of the weighted Wolfsberg–Helmholz formula[7] at $R = d_0$.

$$H_{ij} = \tfrac{1}{2} K S_{ij} [H_{ii} + H_{jj}]$$

$$K = (1 + \kappa) + \Delta^2 - \Delta^4\kappa; \quad 1 + \kappa = 1.75$$

$$\Delta = \frac{H_{ii} - H_{jj}}{H_{ii} + H_{jj}} \qquad (15)$$

Applying (15), eq 12a can be written as follows:

$$K = 1 + (\kappa + \Delta^2 - \Delta^4\kappa) \exp[-\delta(R - d_0)] \qquad (12c)$$

δ is positive. As a consequence, K increases with decreasing interatomic distances, as it should be.

After introducing the corrected distance-dependent Wolfsberg–Helmholz formula, we now briefly discuss the electrostatic two-body interaction $E_{\alpha\beta}(R)$. In his original paper, Anderson introduced the electrostatic energy to describe the interaction $E_\beta(R_\alpha)$ of nucleus α with the neutral atom β in a nonsymmetrical way using the electron density of the more electronegative atom only. This deficiency can easily be corrected by taking the arithmetic mean:[16,22,23]

$$E_{\alpha\beta}(R) = \tfrac{1}{2}[E_\alpha(R) + E_\beta(R)] \qquad (16)$$

Equation 16 can be written as follows:

$$E_{\alpha\beta}(R) = \frac{Z_\alpha Z_\beta}{R} - \frac{1}{2}\left[Z_\alpha \int \frac{\rho_\beta}{|R - r|} \, dr + Z_\beta \int \frac{\rho_\alpha}{|R - r|} \, dr \right] \qquad (17)$$

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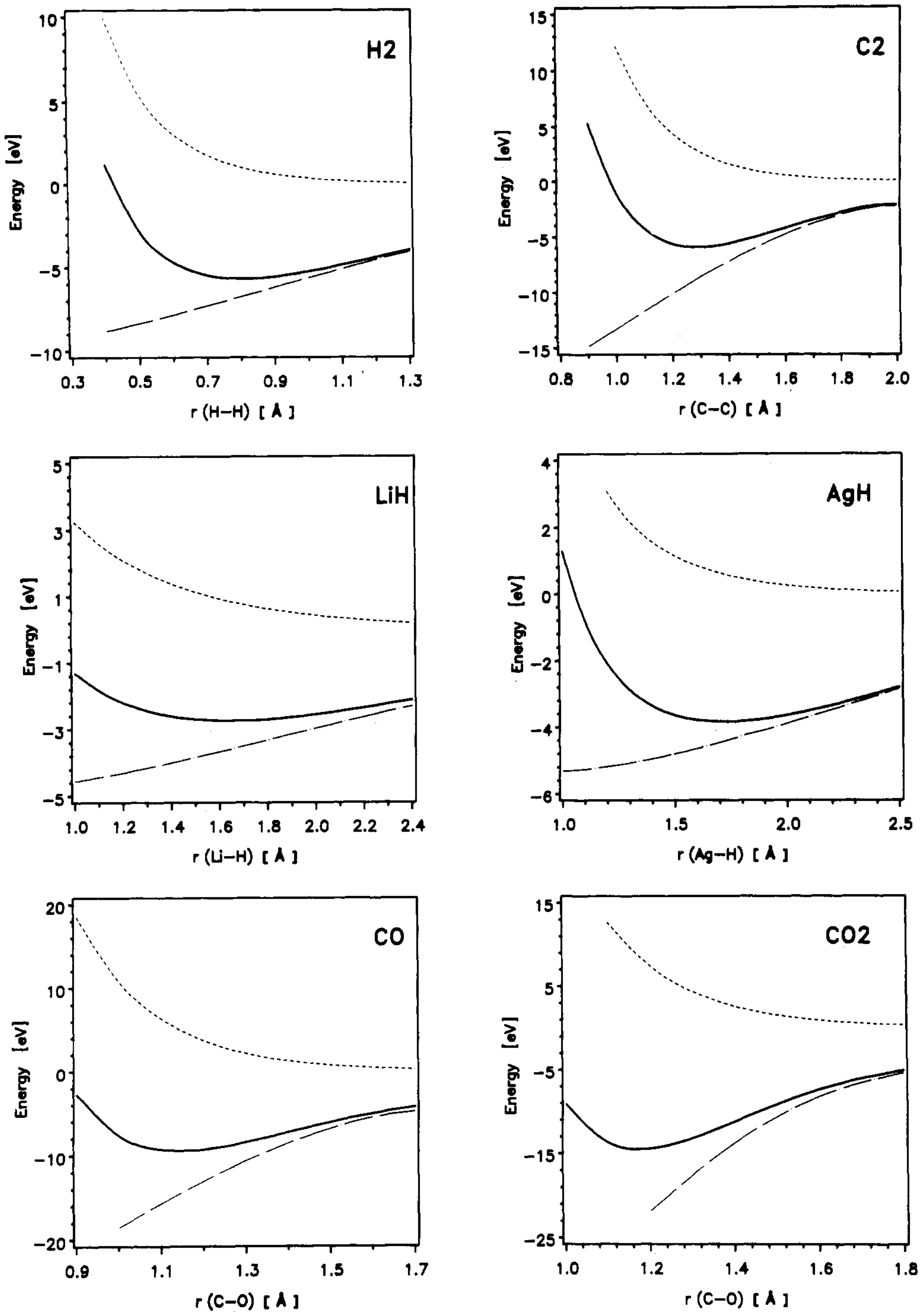

Figure 2. Theoretical results for some diatomic molecules and for the linear CO_2: (···) two-body interaction $E_{\alpha\beta}(R)$; (- - -) $\Delta E_{\mathrm{EHMO}}(R)$; (—) $\Delta E_{\mathrm{EHMO}}(R) + E_{\alpha\beta}(R)$.

Z_α and Z_β are the core charges of the centers α and β. In the Appendix we show that the integrals for STO-type atomic wave functions can be expressed as follows:

$$\int \frac{\rho_\beta}{|R-r|}\,\mathrm{d}r = \frac{1}{R}\sum_{nl} b_{nl}\left[1 - \frac{\exp(-2\zeta_{nl}R)}{nl}\sum_{p=1}^{2n}(2R\zeta_{nl})^{2n-p}\frac{p}{(2n-p)!}\right] \quad (18)$$

nl stands for the principal and the azimuthal quantum numbers, ζ_{nl} is the Slater exponent, and b_{nl} is the occupation number.

4. Comparison with Experimental Results

Let us compare some of the theoretical results with experimental data to get an impression of the results that can be obtained by applying eq 12a for the off-diagonal elements and eq 17 for the two-body electrostatic interactions. Charge iteration was carried out at each point to generate the presented data, applying the parameters from ref 24 and for Ag the ones from ref 25. Slater exponents have been taken from Burns[26] and for Ag from Basch and Gray.[27] Mulliken population analysis was applied.[28] The experimental data reported in Tables I and II originate from ref 19–21 and 29, 30.

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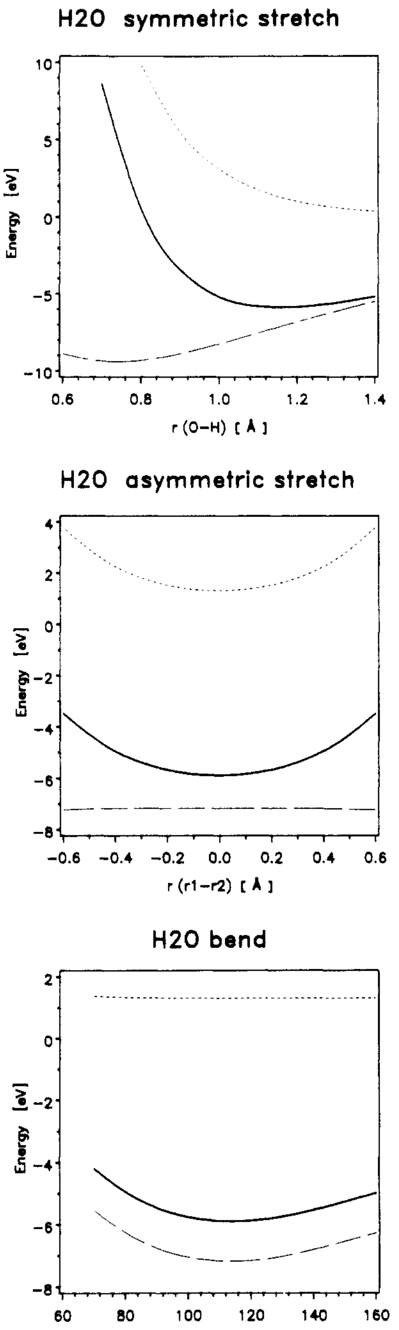

Figure 3. Theoretical results for the three normal modes of H_2O: (···) two-body interaction $E_{\alpha\beta}(R)$; (- - -) $\Delta E_{\text{EHMO}}(R)$; (—) $\Delta E_{\text{EHMO}}(R) + E_{\alpha\beta}(R)$.

In Table I, we report calculated data on diverse diatomic molecules, applying $1 + \kappa = 1.75$ and $\delta = 0.13$.[31] Since it is not possible to use charge iteration on homonuclear diatomic molecules, we have corrected for electron correlation according to Scheme I by adding 1.5 eV to H_{ss}. Bond lengths and first ionization potentials are reasonably well represented by these calculations. The HOMO and the LUMO lead to the correct ground states and to the correct first electronically excited singlet states. This means that they represent a good basis for perturbation theory. Dissociation energy and bond length of CO and SiO are badly represented, and the calculated D_0 of Li_2 and Ag_2 is twice too large.

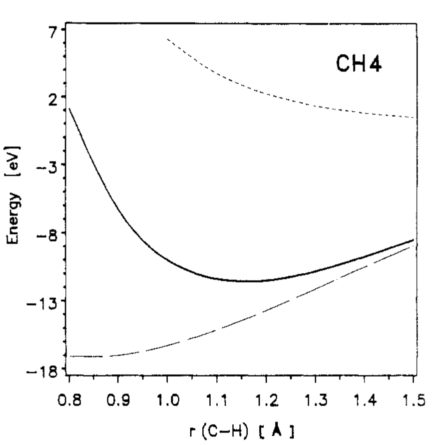

Figure 4. Theoretical results for the symmetric stretching mode of CH_4: (···) two-body interaction $E_{\alpha\beta}(R)$; (- - -) $\Delta E_{\text{EHMO}}(R)$; (—) $\Delta E_{\text{EHMO}}(R) + E_{\alpha\beta}(R)$.

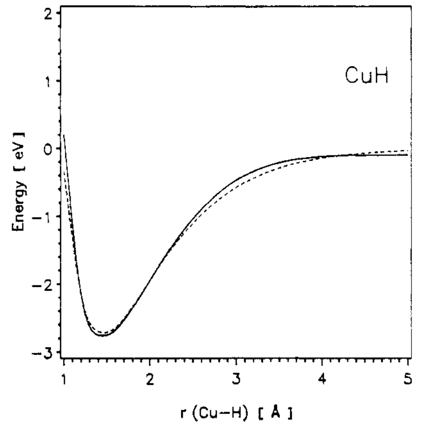

Figure 5. Comparison of the CuH Morse potential with the calculated potential energy curve: (···) Morse potential; (—) optimized parameters ($1 + \kappa = 1.57$ and $\delta = 0.1$).

In the case of the polyatomic molecules in Table Ib, the equilibrium geometry was obtained by independently optimizing bond lengths and valence angles with respect to the energy minimum, thus representing the true minimum on the energy hypersurface. It is well-known that bond angles and first ionization potentials are well-represented by EHMO calculations. Inclusion of the two-body interaction $E_{\alpha\beta}(R)$ also leads to good bond lengths.

In Table II, we present results calculated with $1 + \kappa = 2.0$ and $\delta = 0.35$. The obtained improvement suggests that, for any given class of compounds, a set of κ,δ parameters can be found to describe them with good accuracy.

It is worthwhile to study the energy components $\Delta E_{\text{EHMO}}(R)$, $E_{\alpha\beta}(R)$, and their sum $E(R)$ as a function of bond distances and bond angles; see Figures 2–4. The five diatomics H_2, C_2, LiH, AgH, and CO demonstrate that a reasonable potential energy curve cannot be obtained without inclusion of the electrostatic two-body interaction. Similar results have already been reported by Anderson[8,10–15] although our curves are more satisfactory. The symmetric stretching modes of CO_2, H_2O, and CH_4 demonstrate the great improvement obtained by our approach, while the bending modes, only shown for H_2O in Figure 3, are not markedly influenced by $E_{\alpha\beta}(R)$.

The quality of the calculated potential energy curves can be tested by comparing them with Morse potentials derived from experimental parameters. Such a comparison is made in Figure 5 for CuH. The result is typical for closed-shell configurations

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of molecules. It demonstrates that Morse potentials can be reasonably well simulated if the parameters are optimized. Alkali-metal dimers show a less satisfactory agreement while in many other cases it is even better. This is very interesting because it shows that the general behavior of the EHMO approach, including a two-body repulsive energy term, is correct.

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Appendix

To derive eq 17, let us start with $E_\beta(R)$. With Z_α and Z_β for the core charges, we can write

$$E_\beta(R) = Z_\alpha\left[\frac{Z_\beta}{R} - \int_0^\infty \frac{\rho_\beta(r)}{|R-r|}\,\mathrm{d}r\right]$$

Integrals of this kind can be written as follows:[32]

$$\int_0^\infty \frac{\rho_\beta(r)}{|R-r|}\,\mathrm{d}r = \frac{1}{R}\int_0^R \rho_\beta(r)\,\mathrm{d}r + \int_R^\infty \frac{\rho_\beta(r)}{r}\,\mathrm{d}r = A + B$$

$$\rho_\beta(r) = \sum_{nl} b_{nl}\chi_{nl}{}^2 4\pi r^2$$

b_{nl} is the occupation number of the atomic orbitals of the principal quantum number n and the azimuthal quantum number l. χ_{nl} denotes the Slater-type atomic orbitals.

$$\chi_{nl} = \frac{N_{nl}}{(4\pi)^{1/2}} r^{n-1} e^{-\zeta_{nl}r}; \quad N_{nl} = \frac{(2\zeta_{nl})^{n+1/2}}{((2n)!)^{1/2}}$$

$$\chi_{nl}{}^2 = \frac{(2\zeta_{nl})^{2n+1}}{4\pi(2n)!} r^{2(n-1)} e^{-2\zeta_{nl}r}$$

$$A = \frac{1}{R}\sum_{nl} b_{nl}\int_0^R \chi_{nl}{}^2 4\pi r^2\,\mathrm{d}r = \frac{1}{R}\sum_{nl} b_{nl}\frac{(2\zeta_{nl})^{2n+1}}{(2n)!}\int_0^R r^{2n} e^{-2\zeta_{nl}r}\,\mathrm{d}r$$

$$B = \sum_{nl} b_{nl}\int_R^\infty \frac{\chi_{nl}{}^2}{r} 4\pi r^2\,\mathrm{d}r = \sum_{nl} b_{nl}\frac{(2\zeta_{nl})^{2n+1}}{(2n)!}\int_R^\infty r^{2n-1} e^{-2\zeta_{nl}r}\,\mathrm{d}r$$

$$A + B = \sum_{nl} b_{nl}\left[\frac{1}{R}\frac{(2\zeta_{nl})^{2n+1}}{(2n)!}\int_0^R r^{2n} e^{-2\zeta_{nl}r}\,\mathrm{d}r + \frac{(2\zeta_{nl})^{2n+1}}{(2n)!}\int_R^\infty r^{2n-1} e^{-2\zeta_{nl}r}\,\mathrm{d}r\right]$$

Applying

$$\int x^m e^{ax}\,\mathrm{d}x = e^{ax}\sum_{p=0}^{m}(-1)^p \frac{m!\,x^{m-p}}{(m-p)!\,a^{p+1}}$$

leads to

$$A' = -\frac{e^{-2\zeta_{nl}R}}{R}\sum_{p=0}^{2n}\frac{R^{2n-p}}{(2n-p)!}(2\zeta_{nl})^{2n-p} + \frac{1}{R}$$

$$B' = \frac{e^{-2\zeta_{nl}R}}{2nR}\sum_{p=0}^{2n}\frac{R^{2n-p}}{(2n-p)!}(2\zeta_{nl})^{2n-p}(2n-p)$$

$$A' + B' = \frac{1}{R} - \frac{e^{-2\zeta_{nl}R}}{2nR}\sum_{p=1}^{2n}(2R\zeta_{nl})^{2n-p}\frac{p}{(2n-p)!}$$

Therefore we have

$$\int_0^\infty \frac{\rho_\beta(r)}{|R-r|}\,\mathrm{d}r = \sum_{nl} b_{nl}\left[\frac{1}{R} - \frac{e^{-2\zeta_{nl}R}}{2nR}\sum_{p=1}^{2n}(2R\zeta_{nl})^{2n-p}\frac{p}{(2n-p)!}\right]$$

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Molecular Inversion Dynamics of Bis(cyclopentadienyl)beryllium Inferred from Partially Relaxed Spin–Spin Coupling between Carbon-13 and Beryllium-9

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The rate of molecular inversion of bis(cyclopentadienyl)beryllium is estimated to be $10^{10\pm1}$ s^{-1} in diethyl ether or cyclohexane solutions at room temperature. Inversion occurs by the interchange of the central (η_5) and peripheral (η_1) bonding roles of the two cyclopentadienyl rings and causes the hydrogen and the carbon atoms each to be dynamically averaged in their respective NMR spectra. The ^{13}C spectra display fine structure, however, which arises from incomplete decoupling from the quadrupolar ^{9}Be nucleus ($I = {}^3/_2$). The ^{1}H-decoupled ^{13}C spectrum is a narrow doublet which collapses to a singlet as the temperature is lowered, with an apparent activation energy of 5.2 kJ mol^{-1}. The line shape is independent of the magnetic field strength between 2.1 and 9.4 T and does not change significantly between the two solvents. These observations lead to the conclusion that the relaxation of the ^{9}Be nucleus is predominantly caused by the molecular inversion and not by molecular tumbling. A precise value for the inversion rate cannot be calculated in the absence of the nuclear quadrupole coupling constant.

Introduction

The ^{1}H NMR spectrum of bis(cyclopentadienyl)beryllium ($BeCp_2$) in solution is a singlet, even at −135 °C.[1-3] Yet the molecule is polar in solution.[4] This excludes the symmetrical ferrocene structure (Figure 1a) and implies that the equivalence of all of the protons in the NMR spectrum is the consequence of some dynamical averaging process. The ^{9}Be NMR spectrum is also a singlet at room temperature,[1] as would be expected for any of the structures which have been proposed for the molecule (Figure 1).

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