Non-empirical SCF Calculations on Hydrogen-like Molecules: the Effect of Nuclear Charge on Binding Energy and Bond Length

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Summary Non-empirical calculations on hydrogen-like molecules with nuclear charges different from unity lead to a derivation of Pauling's relationship between bond energy and electronegativity differences; they also show that a bond may be strengthened by effective positive charges on adjacent nuclei provided the charges are not too large.

MOLECULES containing two nuclei and two electrons may be referred to as hydrogen-like molecules by analogy with hydrogen-like atoms containing a single electron. Hydrogen-like molecules can serve as useful models for studying the properties of two-electron bonds in more complex molecules. In particular,[1] changes in bond properties due to the screening effects of electrons not involved in the bond under consideration can be simulated by varying the nuclear charges in hydrogen-like molecules.

We report some results of non-empirical SCF calculations using an extended basis set of Gaussian type orbitals[2] (6*s*, 4*px* for each nucleus) for heteronuclear and homonuclear hydrogen-like molecules. For H_2 (see Table) (1·0; 1·0) the calculated molecular energy $-E_T = 1{\cdot}1329$ H is within 0·001 H of the Hartree–Fock limit $-E_T = 1{\cdot}1336$ H.[3] The electronic correlation energy, which should be added to the Hartree–Fock energies, is $-0{\cdot}041$ H for H_2 and $-0{\cdot}042$ H for He[4] (2·0; 0) so it is probably practically the same for all hydrogen-like molecules. The calculated value of R_0 for H_2 agrees closely with the experimental value. This is the only case where comparison is possible.

For the heteronuclear hydrogen-like molecules ($1 + \delta$; $1 - \delta$) the total molecular energy $-E_T$, the binding energy for dissociation into "atoms" $-E_B = -E_T - (1 + \delta)^2/2 - (1 - \delta)^2/2$, and the internuclear distance R_0 all increase with increasing charge asymmetry. At first sight it may appear puzzling that the increase in binding energy is here associated with lengthening of the bond (and with a lowering of the force constant). However, it is clear that for the (2·0, 0·0) molecule, consisting of a He atom plus a "nucleus" of zero charge, the "binding energy" as defined is just the energy associated with the ionization process $He \rightarrow He^+ + e^-$. If we had defined the binding energy of H_2 with respect to dissociation into H^- and H^+ the corresponding quantity would decrease with increasing charge asymmetry, becoming zero for the (2·0, 0·0) molecule.

TABLE

Summary of results for hydrogen-like molecules

Z_A; Z_B	1·0; 1·0	1·2; 0·8	1·4; 0·6	1·6; 0·4	1·8; 0·2
$-E_T$(H)	1·1329	1·2026	1·4120	1·7602	2·2450
$-E_B$(H)	0·1329	0·1626	0·2520	0·4002	0·6050
R_0(B)	1·39	1·405	1·45	1·55	1·80

Z_A; Z_B	0·8; 0·8	1·0; 1·0	1·2; 1·2	1·4; 1·4	1·6; 1·6	1·8; 1·8	2·0; 2·0
$-E_T$(H)	0·7175	1·1329	1·5920	2·0778	2·5779	3·0840	3·5922
$-E_B$(H)	0·0775	0·1329	0·1520	0·1178	0·0179	−0·1560	−0·4078
R_0(B)	1·54	1·39	1·31	1·27	1·25	1·26	1·30

The Hartree–Fock energy of the He atom is −2·8617 H,[5] and the calculated energies of the ($1 + \delta$; $1 - \delta$) molecules are found to be given very closely by the expression $-E_T^{HF}(1 + \delta;\ 1 - \delta) = -E_T^{HF}(1{\cdot}0;\ 1{\cdot}0) + 1{\cdot}728\,\delta^2$. The conventional binding energies are then $-E_B^{HF}(1 + \delta;\ 1 - \delta) = -E_B^{HF}(1{\cdot}0;\ 1{\cdot}0) + 0{\cdot}728\,\delta^2$ where $\delta^2 = (Z_A - Z_B)^2/4$. This is analogous to Pauling's empirical formulae (1) and (2) relating bond energies (in kcal/mol) to electronegativity differences.[6]

$$D(A-B) = 0{\cdot}5[D(A-A) + D(B-B)] + 23(x_A - x_B)^2 \qquad (1)$$

or

$$D(A-B) = [D(A-A)\cdot D(B-B)]^{1/2} + 30(x_A - x_B)^2 \qquad (2)$$

Since electronegativity is defined in a general way as the power of an atom in a molecule to attract electrons to itself, our result can be regarded as a non-empirical derivation of Pauling's formula for hydrogen-like atoms. Instead of the geometric mean (or arithmetic mean) of the bond energies strictly we should take the energy of a homopolar bond between atoms of mean electronegativity, a quantity that is not readily available from experimental data.

The calculations on the homonuclear molecules ($1 \pm \delta$; $1 \pm \delta$) confirm some earlier conclusions obtained by Cottrell and Sutton[1] on the basis of the Heitler–London model. As the nuclear charges are increased from unity, the total molecular energy $-E_T$ and the binding energy $-E_B$ increase while the internuclear distance R_0 decreases. We find that the binding energy reaches a maximum value of 0·153 H at δ 1·17,[7] the bond length a minimum value of 1·25 B at δ ~ 1·6. For He_2^{2+} (2·0; 2·0) our calculated value of $-E_T$ is 3·5922 H at R_0 1·30 B, corresponding to a metastable molecule, in qualitative agreement with previous results.[8] Use of the He basis set[2] (6*s*, 4 *px* uncontracted GTO) lowers E_T to −3·5958 H without change in R_0. In general, calculations made with different basis sets (H, He, interpolated coefficients) give slightly different numerical values but do not change any of the qualitative results. We conclude therefore that in hydrogen-like molecules a fractional increase in nuclear charge leads to stronger bonding and to a decrease of the equilibrium internuclear distance.

Although the concept of effective nuclear charge has no strict quantum mechanical foundation, it is useful in discussing the properties of more complex molecules. An increase in the effective nuclear charges of a pair of bonded atoms can be achieved by introducing electronegative substituents or by the presence of neighbouring cations which, by withdrawing electrons from the atoms in question, reduce the nuclear screening for the bonding electrons. The exact outcome will depend on a rather delicate balance of several effects and cannot possibly be predicted at this level of argument. However, when bond-shortening is actually observed following introduction of electronegative substituents or neighbouring cations, it may be attributed, in the absence of other causes, to increase in effective nuclear charge of the atoms involved in the bond.

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[7] The value δ 1·17 for maximum bonding energy is, not unexpectedly, close to the values derived for the "effective nuclear charge" in early variational treatments of the H_2 molecule, *e.g.* S. Wang, *Phys. Rev.*, 1928, **31**, 579.

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