On an Ionic Approximation to Homonuclear Bonding

G. Van Hooydonk
Rijksuniversiteit te Gent, Centrale Bibliotheek, Gent, België

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An ionic, i.e. basicly an electrostatic, approximation to homonuclear bonding between several monovalent atoms is examined. A simple correlation seems to exist between molecular constants (bond length and bond energy) and atomic constants (ionization energy and electron affinity). Bond stability is explained in terms of a saturation of the electron affinities of the bonding partners.

1. Introduction

An explanation of the stability of homonuclear two-center two-electron bonds with the use of an ionic approximation is difficult for various reasons. Even before the advent of quantumchemistry, the electrostatic approach to homonuclear bonding was abandonned[1], since the simple electrostatic considerations involved led to erroneous results for several interesting cases, among which the hydrogen and halogen homonuclear diatomic bonds are striking examples.

Homonuclear bonding was given a first quantummechanical explanation by Heitler and London[2], but it must be realized that, in spite of the enormous progress made along these lines, quantumchemistry is still left with the problem of describing unambiguously the contribution of ionic structures to the ground state of homonuclear bonds. This is clearly seen when one compares the original V.B. and M.O. (and various intermediate) approaches to account for chemical bonding. In view of the historical development in the attempts to explain homonuclear bonding, this is a very unfortunate situation.

Therefore, the present report is devoted to a reconsideration of an ionic, i.e. basicly an electrostatic, approximation to homonuclear bonding.

2. The Ionic Approximation to Homonuclear Bonding at the Equilibrium Internuclear Distance

The ionic approximation to bonding in an homonuclear two-center two-electron bond A_1A_2 starts from the wave function:

$$\psi_{A_1A_2} = \psi_{A_1}(1)\,\psi_{A_1}(2) + \psi_{A_2}(1)\,\xi\,\psi_{A_2}(2) \qquad (1)$$

which, as a working hypothesis, is assumed to be valid at the equilibrium internuclear distance $r = r_{0\mathrm{AA}}$. This combination of ionic orbitals was for instance also considered by Heitler and London[2], but was rejected as a possible solution for their problem for various reasons of a rather qualitative nature.

With assumption (1), one can simplifyingly discuss a single solution corresponding, for instance, with a structure $A_1^+A_2^-$. The consideration of only one-center two-electron problems in this way greatly simplifies the formal solution of the wave equation, since one directly obtains for the total energy $\varepsilon_{A_1+A_2-}$ at the equilibrium internuclear separation:

$$\varepsilon_{A_1+A_2-} = IE_A + EA_A + e^2/r_{0\mathrm{AA}} \qquad (2)$$

if only valence electrons are considered. Hereby IE_A and EA_A stand, respectively, for the ionization energy and the electron affinity of atom A and the point charge (hard sphere) approximation is assumed to be valid in first instance.

If the combination AA at $r_{0\mathrm{AA}}$ is stabilized with respect to the two separated neutral atoms by the amount E_{AA}, the bond energy, the validity of the ionic approximation implies that at the equilibrium separation:

$$IE_A + EA_A + e^2/r_{0\mathrm{AA}} = 2\,IE_A + E_{\mathrm{AA}} \qquad (3)$$

or,

$$E_{\mathrm{AA}} = EA_A + e^2/r_{0\mathrm{AA}} - IE_A \qquad (4)$$

and the interpretation of this Eq. (4) is of considerable interest for any further discussion of an ionic approximation.

Indeed, if for instance E_{AA} and EA_A were identical, as suggested earlier[3], a further consequence of this approximation would be that $IE_A = e^2/r_{0\mathrm{AA}}$.

The experimental values for these two sets of atomic and molecular constants are practically always found in the same range of energy (for a more detailed discussion of individual cases: vide infra).

Reprint requests to Dr. G. Van Hooydonk, Rijksuniversiteit te Gent, Centrale Bibliotheek, Rozier 9, B-9000 *Gent/België.*

As a first consequence of the application of the ionic approximation to homonuclear bonding in its present form, one could therefore assume that all basic information about a *molecule* AA is already contained in the properties of the single *atom* A, i.e.

a) $EA_{\rm A}$ of atom A determines $E_{\rm AA}$ of the bond AA, and

b) $IE_{\rm A}$ of atom A determines $r_{0\rm AA}$ of the bond AA.

Hence, at $r_{0\rm AA}$, the effective ionization energy of atom A_1 is zero (no loss in total energy is observed upon taking away the valence electron of A_1 due to the Coulomb energy available), whereform automatically all net stabilization of the A_1A_2 combination will be due to the saturation of the $EA_{\rm A_2}$ value. The bond energy might then be described in function of EA values only, which would be consistent with our previously introduced modified HMO formalism[3]. It was there shown also that, in order to have a completely ionic bond, the ionization energy of one of the bonding partners has to be zero.

Whereas a two-center one-electron bond is stabilized through the saturation of the cation affinity of a neutral atom, a two-center two-electron bond is stabilized through the saturation of the electron affinity.

This bonding mechanism relies on the fact that the two reactions:

$$A^+ + e^- \rightarrow A\,, \quad A^+ + A^- \rightarrow AA \qquad (5)$$

should be equally exothermic, but this does not account for the observed dissociation process of AA bonds, leading to neutral atoms A instead of ions A^+ and A^-. Even when at $r = r_{0\rm AA}$ the ionic approximation would be valid, it completely fails to describe the interaction of two neutral atoms at larger r-values, especially at $r = \infty$, where the Heitler-London non ionic function is exactly valid.

3. The Ionic Approximation to Homonuclear Bonding at non Equilibrium Internuclear Separation

Any approximation to chemical bonding should also account for the observed alterations in electronic energy with decreasing internuclear separation, i.e. it should allow one to construct potential energy curves, consistent with experimental observation.

A combination of originally separated ions A^+ and A^- gives a critical distance $r_{\rm c} = (IE_{\rm A} - EA_{\rm A})/e^2$ at which this combination has the same total energy as two neutral atoms A at infinite internuclear separation. Experimental observation however suggests that, at $r_{\rm c}$, a combination of neutral atoms A is already largely stabilized with respect to the $2\,IE_{\rm A}$ starting energy level. Nevertheless, a consideration of only ionic structures at $r = r_{0\rm AA}$ does not necessarily imply that the ions are retained as such upon increasing internuclear separation, which may be seen from a reverse argumentation.

Indeed, for a combination of neutral atoms A_1 and A_2 at any distance r, it is readily seen that "partial" ionization of either one of the two atoms is energetically possible without loss of energy, due to the Coulomb attraction energy e^2/r available at that r-value.

Hence, we will put for any r-value:

$$IE_{\rm A_1} = IE_{\rm A_1}(r) + e^2/r \qquad (6)$$

indicating that there is, also energetically, a finite probability of finding the valence electron of A_1 at A_2. As a result, this process will cause the $EA_{\rm A_2}$ value to be gradually saturated, leading to stabilization with respect to the $2\,IE_{\rm A}$ level also, even at $r > r_{\rm C}$. At $r = r_{0\rm AA}$, $IE_{\rm A}\,({}_1r) = 0$, and a total amount of energy, equal to $EA_{\rm A_2}$ is set free, corresponding to the bond energy of the chemical combination AA.

Even in the absence of an external attractive force at A_2, there is always a certain probability of finding the valence electron of A_1 at distances, larger than its atomic radius, which is easily verified upon inspecting the radial part of the atomic wave function.

The ionic approximation then transforms the problem of accounting for the increasing stability of an AA combination with decreasing r values, to the one of accounting for a gradual saturation of the electron affinity upon decreasing r values, which results in a separation of "atomic" and "molecular" energy alterations upon decreasing internuclear distance.

Incorporation of the variable distance r between two neutral atoms A_1 and A_2 then leads to:

$$E_{\rm A_1A_2}(r) = \varepsilon_{\rm A_1A_2}(r) - \varepsilon_{\rm A_1A_2}(\infty)\,, \qquad (7)$$

$$= IE_{\rm A_1}(r) + e^2/r + IE_{\rm A_2} + EA_{\rm A_2}(r) - IE_{\rm A_1} - IE_{\rm A_2} \qquad (8)$$

which, on account of assumption (6), reduces to:

$$E_{\rm A_1A_2}(r) = EA_{\rm A_2}(r)\,. \qquad (9)$$

For a combination A^-, originating from the interaction between a neutral atom A and an electron, the following general relation, taken from atomic energy calculations, may be written down[4]:

$$\varepsilon_{A^-}(R) = a/R - b/R^2 \qquad (10)$$

where R denotes the separation between the electron and nucleus A. Equation (10) is just a combination of the potential (a/R) and kinetic (b/R^2) energy of the electron and their expectation values depend on the effective nuclear charge of A (corrected for shielding by its valence electron also), which is related to the coefficient of $1/R$.

Minimization yields that, at $R = R_0$, $b = (1/2)a\,R_0$, satisfying the virial theorem for $\varepsilon_{A^-}(R_0)$, wherefrom, in terms of $\varepsilon_{A^-}(R_0)$ there results, instead of Equation (10):

$$\varepsilon_{A^-}(R) = EA_A(2\,R_0/R - R_0^2/R^2) \qquad (11)$$

since the expectation value $\varepsilon_{A^-}(R_0) = EA_A$. This equation is similar to the one describing the same saturation process in function of a partial charge transfer q, as evaluated from purely electrostatic considerations by Ferreira[5], i.e.

$$\varepsilon_{A^-}(q) = EA_A(2\,q - q^2) \qquad (12)$$

although for the latter equation the boundary values $0 < q < 1$ should be imposed.

If however the approaching electron is not originally free but belongs to another atom A, one should for instance express the saturation process of EA_A in function of the internuclear separation r, which is not identical with R.

Anyhow, within the ionic approximation, the saturation will also be maximum at $r = r_{0AA}$ and zero for $r = \infty$, but for intermediate cases the situation is not clear.

Hence, without knowing the exact dependence on r explicitly, one can simplifyingly assume that, around r_{0AA}, the following relation should hold according to the requirements of the ionic approximation:

$$E_{A_1A_2}(r) = (-EA_A)\,(1 - r_{0AA}/r)^2 \qquad (13)$$

which is obtained from Eq. (11) after substituting for r and rewriting for a zero energy level at r_{0AA} (oscillator representation).

For small deviations around r_{0AA}, Eq. (13) may be transformed into:

$$E_{A_1A_2}(r) = (-EA_A)\,[1 - \exp\{-(r - r_{0AA})/r\}]^2 \qquad (14)$$

which must be considered only as a first approximation to the actual stabilization process for a combination of neutral atoms according to the ionic approximation. It is of course possible to consider other transformations, having the same boundary conditions also, but, if we base our further discussion on Eq. (14) as an example, it is seen that the probability of finding the valence electron of A_1 at A_2 for intermediate r-values depends exponentially on

$$(IE_{A_1} - e^2/r)\,/\,(e^2/r) \qquad (15)$$

which, in the ionic approximation, has a definite physical meaning.

Hence, formal evidence towards the validity of the present approach is offered by a comparison of Eq. (14) with Morse's empirical potential energy curve[6] for "neutral" atoms:

$$E_{AA}(r) = D_{AA}[1 - \exp\{-a(r - r_0)\}]^2 \qquad (16)$$

when it is reminded that according to the present approach $-EA_A = D_{AA}$. The form of both curves will however only be identical provided $a = r_{0AA}^{-1}$ and $r_0 = r_{0AA}$. Morse's parameter a is obtained through experimentally observed data and it will, as such, reflect the influence of other effects, such as repulsive ones, also.

Nevertheless, the crude approximation of considering only the extra potential energy $(\propto r^{-1})$ and the extra kinetic energy $(\propto r^{-2})$ of the approaching valence electron, in first instance justified by an ionic approach to bonding, leads to a form of the $E_{AA}(r)$ curve already qualitatively conform with experiment, especially with the requirement that the allowed vibrational energy levels be given, in first approximation, by a finite polynomial. It must however be reminded that r_0 in Morse's formula is the experimentally observed equilibrium distance, whereas, according to the present approach, r_{0AA} is the predicted expectation r-value, at which there is just enough internuclear Coulomb energy available to allow complete ionization of one of the bonding partners to take place.

As soon as for instance there are external disturbing forces (i.e. forces not residing in the valence electrons) of repulsive nature, complete ionization cannot take place, and, correspondingly, the electron affinity cannot be saturated completely. Although, in principle, repulsive effects may conveniently be taken into account by adding terms in r^{-n} $(n \geqq 1)$ or in $\exp\{-r\}$ in the potential energy expression, we have preferred to compare the rather "ideal" molecular constants, as predicted by the present simplified version of the ionic approximation, with experimental data. Indeed, with the use of the simple rule, given in Sect. 2, it should be possible to make predictions for almost any homonuclear diatomic bond, provided the ionization energy and the electron affinity of the bonded atoms are known. In how far these predictions are conform with experimental observation is discussed in the next section.

4. Results and Comments

1. *Molecular constants obtained from atomic constants*

The predicted and observed molecular constants for several homonuclear AA bonds have been collected in Table 1. A first glance at this Table shows that in the case of alkalimetals there is substantial evidence for the ionic approximation to homonuclear bonding to be valid, even quantitatively, although some values are only tentative. These findings are conform with our earlier statement that the alkali metals show a relatively "ideal" chemical behaviour[7]. The observed larger equilibrium distances for Na, K, Rb and Cs might be ascribed to polarization effects, which, on the whole, are relatively small, as are, for instance, also Born repulsion forces. The fact that r_{obs} slightly exceeds r_{calc} will cause the EA_{A} value not be to completely saturated (Sect. 3), although it is difficult to treat this effect quantitatively. The EA_{Li} seems to be low, since in this case the r_{obs} value is exactly reproduced. It may be noticed hereby that, according to the approximate formulae given in Sect. 3, small deviations around r_{calc} will only have a minor effect upon the saturation of the EA value, wherefrom $EA_{\text{A}} \approx E_{\text{AA}}$ as observed in these cases.

Table 1. Predicted and observed molecular constants for several homonuclear bonds between monovalent atoms.

Bond AA	r_{calc}[a] (Å)	r_{obs}[b] (Å)	$E_{\text{AAcalc}} = EA_{\text{A}}$[b] (eV)	E_{AAobs}[b] (eV)
LiLi	2.67	2.67	0.62	1.08
NaNa	2.80	3.08	0.84	0.75
KK	3.32	3.92	0.69	0.51
RbRb	3.44	(4.1)	(0.6)	0.47
CsCs	3.70	(4.3)	(0.5)	0.45
FF	0.83	1.42	3.48	1.56
ClCl	1.11	1.99	3.69	2.48
BrBr	1.22	2.28	3.49	1.97
II	1.37	2.67	3.21	1.54
HH	1.06	0.74	0.7[c]	4.48

[a] Calculated from $r_{\text{AA}} = IE_{\text{A}}/e^2$, with the use of IE_{A} values given in C. E. Moore, Atomic Energy Levels, Nat. Bur. Stand., Washington D.C. 1949.

[b] All values taken from a compilation by G. Klopman, J. Amer. Chem. Soc. **86**, 1463, 4550 [1964] unless otherwise indicated, including those between brackets, which are estimated values.

[c] See Reference 11, 12.

For halogens, a large discrepancy is found between predicted and observed molecular constants. Obviously, the presence of lone electron pairs on both the bonding partners in these cases[7,8], accounts, in first instance, for the fact that $r_{\text{obs}} \gg r_{\text{calc}}$. Since now the deviation from r_{calc} is quite large, the electron affinity can only be partly saturated (vide supra), leading to $E_{\text{AA}} < EA_{\text{A}}$ in these cases, as observed.

Whereas this situation for halogens is frequently referred to [1,9] as being unsatisfactory enough to reject an explanation for homonuclear bonding in terms of an ionic approximation, the present treatment shows that halogens are, at least, badly choosen examples to discuss this topic due to the large — essentially disturbing — non bonding effects present in these cases. The present ionic approach to homonuclear bonding is indeed not in conflict with experimental observation for halogen-halogen bonds.

Although in the case of hydrogen there is enough Coulomb energy available at r_{obs} to allow either one of the two bonding partners to be ionized, the fact that, only in this case, r_{obs} is smaller than r_{calc} needs further consideration.

Indeed, a calculation of E_{HH} with the use of Eq. (4) gives a bond energy in agreement with experiment (4.8 eV) if the calculated EA_{H} value[10] is thereby used. Nevertheless, if the rule, applied above for the evaluation of molecular constants, is applied in the case of hydrogen, large discrepancies are found (see Table 1), due to the fact that r_{HH} is much smaller than 2 × the Bohr radius and that $EA_{\text{H}} \ll E_{\text{HH}}$.

Since externally disturbing effects, such as those considered above are absent in H_2 and even Born repulsion could tacitly be neglected in the former cases, a consideration of both the particularly low r_{obs} and the relatively low value for the Born repulsion exponent for hydrogen n_{H}, indicates that this type of repulsion might be appreciable. Indeed, in order for complete ionization to take place in hydrogen, there would then result:

$$e^2(1 - 1/n_{\mathrm{H}})/r_{0\mathrm{HH}} = IE_{\mathrm{H}} \qquad (17)$$

leading to $r_{\mathrm{calc}} = 0.795$ Å to be compared with r_{obs}, when it is tentatively assumed that $n_{\mathrm{H}} = 4$[11].

Assuming that then this part of the rule, given above, is not in conflict with experimental observation, we are left with the drastic discrepancy between EA_{H} and E_{HH}, the predicted and observed bond energy respectively.

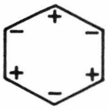
With respect to this rather ambiguous sitation for hydrogen, it is most unfortunate that the EA_{H} value, which has been obtained through extremely refined quantummechanical calculations[10, 12], could not yet be confirmed through experimental observation (see however Ref. [12]) and this remark is valid for electron affinity values in general, since these are not easily accessible.

If we regard the calculated EA_{H} value as correct, the hydrogen bond seems to be the only case, among the homonuclear bonds thus far considered, in which the simple rule for the evaluation of molecular constants, cannot be applied. Nevertheless, this discrepancy can hardly be taken as evidence against the ionic approximation in general, since equation (4) is still obeyed.

2. *Further applications of the ionic approach to homonuclear bonding*

As soon as the energetical barrier against the ionic approximation might be removed, a number of interesting chemical applications can be made. Indeed, a description of an assembly of homonuclear bonds largely depends on how individual homonuclear bonds are described.

A specific example is the situation in the benzene molecule, where one is faced with a particular configuration of homonuclear bonds. Leaving the validity of the σ-π separation aside for the moment, one obtains for the π-electron system in the benzene molecule, accodring to the ionic approximation, the following representation:



which, at once, removes several difficulties inherent to the Kékulé benzene structures (non-existence of two X_2-ortho-derivatives).

Moreover, in singly substituted benzenes, ortho- and para-places are linked together (same sign of the charges) and if the preference of substituents for electron-rich or electron-poor domains is taken into account, this representation might justify, energetically, several of the commonly accepted mechanisms to account for the reactivity of aromatic compounds and of unsaturated hydrocarbonds in general.

Another interesting arrangement of homonuclear bonds is found in pure metals. As an illustration, we give the interaction of a pair of Li_2-molecules:

$$\begin{array}{ccccc} \mathrm{Li}^+ & & \mathrm{Li}^- & & \mathrm{Li}^+ - \mathrm{Li}^- \\ | & + & | & \rightarrow & | \qquad\quad | \\ \mathrm{Li}^- & & \mathrm{Li}^+ & & \mathrm{Li}^- - \mathrm{Li}^+ \end{array}$$

and the similarity with the situation in benzene comes out clearly in the ionic approximation also.

It may be noticed hereby that just in these cases where the simple rule for the prediction of molecular constants holds rather rigorously, the intermolecular interaction, as described above, can be justified, since these atoms (and the corresponding molecules) tend to form metallic aggregates. This is further evidence for the fact that large repulsive forces will be absent in these cases.

5. General Discussion

The results obtained strongly suggest that, for a two-center two-electron homonuclear bond, the Hamiltonian may be reduced, at $r = r_0$, to a one-center two-electron Hamiltonian $H(1, 2)$, similar to the one used for He and He-like ions, with, however, addition of the internuclear Coulomb (stabilizing) potential energy. This is indeed a drastic simplification not easily introduced a priori.

In as far as we may say that a two electron problem can be solved "exactly", an inspection of the two equivalent simplified forms of the Hamiltonian, i.e. $H(1, 2)_{\mathrm{A}_1}$ and $H(1, 2)_{\mathrm{A}_2}$, for an homonuclear bond $\mathrm{A}_1\mathrm{A}_2$, reveals that the wave equations may be solved "exactly" by means of their respective eigenfunctions $\psi_{\mathrm{A}_1}(1)\,\psi_{\mathrm{A}_1}(2)$ and $\psi_{\mathrm{A}_2}(1)\,\psi_{\mathrm{A}_2}(2)$, corresponding with the two terms in Equation (1).

Whereas Heitler and London[2] found an approximative wave function for the hydrogen molecule by considering the simplified form of the Hamiltonian at *infinite* internuclear separation (i.e. they just considered a completely non-bonded unperturbed system, consisting of two independent neutral atoms), the ionic approximation relies upon a simplified form of the Hamiltonian at the *equilibrium* internuclear separation, where — to cite Weisskopf[4] — the Heitler-London theory would not even give a hint about the correct result. The corresponding eigenfunctions, given in the wave function (1), will then describe the situation only around this equilibrium internuclear distance, and, moreover, such an "ionic" state must be given the same term symbol as the Heitler-London non ionic state.

If these two wave functions $\psi(1,2)_{A1}$ and $\psi(1,2)_{A2}$ represent the best solutions for the wave equations at $r = r_{0AA}$, i.e. for the perturbed system, the fact that one has to take into consideration both solutions is only dictated by the symmetry of the problem, and in particular, by the requirement that the ground state has a zero permanent dipole moment: indeed, any of these two eigenfunctions will lead separately to the correct energy. In this way, "exchange forces"[2] can possibly be described in a rather "classical" way! Such explicit dependence on r is not found in other bond theories[13] and the flexibility in the wave function leads to a very simple rule for the prediction of the chemical behaviour of elements.

Although the present formulation of the ionic approximation to homonuclear bonding may seem rather crude, due to the very simple Hamiltonian operator it is based upon, it turns out to be consistent with a number of observed phenomena of a different nature and even, quite unexpectedly, with the interaction of a pair of neutral atoms, as described by Morse's well working empirical formula. Indeed, it directly generates a potential energy curve of the general form:

$$E_{AA}(r) = E_{AA}(2x - x^2) \qquad (18)$$

whereby x is a simple function of r, which, the other way around, can be interpreted as a first rough verification of the present approach.

Whereas it is usually assumed that, at small internuclear separation, the classical hard sphere description for Coulomb attraction forces breaks down, this assumption is clearly in contradiction with the situation in the large number of heteronuclear bonds and in crystals, where, respectively, part of the bond energy and the whole energy can successfully be described with the use of these same forces, operating in a number of such cases at equally small internuclear separations.

The only stumbling block thus far met for the simple rule, proposed in Sect. 2, is the large discrepancy that exists between the calculated EA_H value and the experimentally observed E_{HH} value. Whether or not this is sufficient evidence for the rejection of an ionic approximation in terms of this simple rule, is not yet clear, but it is a very poor basis indeed to condemn any ionic approximation to homonuclear bonding.

In fact, the main problem in a discussion of chemical bonding is not which forces the atoms exert upon each other, since these are essentially of electrostatic nature, but, *how* these forces are to be described. Even a simple hard sphere representation — with its inherent limitations — seems to work reasonably well, even for homonuclear bonds, as shown in this report.

6. Conclusion

An ionic approximation to homonuclear bonding seems not to be in conflict with experimental observation. A simple rule can be derived, which gives molecular constants directly from atomic ones. Definite conclusions about the validity of the present approach can only be reached at when firmly established electron affinity values will be available. A suited introduction of repulsive energies might lead then to an explicit evaluation of the function of r needed to compute potential energy curves satisfactorily. The main point however is the simplification of the Hamiltonian for a two-center two-electron homonuclear bond at the equilibrium distance: whether or not these assumptions may be justified theoretically, remains to be determined.

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[1] A. E. Van Arkel and J. H. De Boer, Chemische Binding als Electrostatisch Verschijnsel, D. B. Centen's Uitg. Maatschappij, Amsterdam 1930.

[2] W. Heitler and F. London, Z. Physik **44**, 455 [1927].

[3] G. Van Hooydonk, Z. Naturforsch. **28a**, 933 [1973].

[4] a) V. Weiskopf in: Lectures in Theoretical Physics (Ed. W. E. Brittin, D. W. Downs and J. Downs), Vol. III, Interscience Publishers Inc., New York 1961. — b) J. C. Slater, Quantum Theory of atomic Structure, Vol. I, McGraw-Hill Book Company Inc., New York 1960.

[5] R. Ferreira, Trans. Faraday Soc. **59**, 1075 [1963].

[6] P. M. Morse, Phys. Rev. **34**, 57 [1929].

[7] G. Van Hooydonk, Theoret. Chim. Acta **22**, 157 [1971].

[8] P. Politzer, J. Amer. Chem. Soc. **91**, 6236 [1969]. — K. S. Pitzer, Adv. Chem. Phys. **2** 59 [1959]. — R. S. Mulliken, J. Amer. Chem. Soc. **72**, 4493 [1950]; **77**, 884 [1955].

[9] L. Pauling, The Nature of the Chemical Bond, Cornell University Press, Ithaca 1960.

[10] H. Bethe, Z. Physik **57**, 815 [1929]. — C. L. Pekeris, Phys. Rev. **112**, 1649 [1958].

[11] Estimated from the Born repulsion exponents for alkalihydrides, given in O. K. Rice, Electronic Structure and Chemical Bonding, McGraw-Hill Book Company Inc., New York 1940.

[12] E. A. Hylleraas, Z. Physik **60**, 624; **63**, 291 [1930].

[13] S. Weinbaum, J. Chem. Phys. **1**, 593 [1933]. — C. A. Coulson and I. Fischer, Phil. Mag. **40**, 386 [1949]. — For lucid accounts on VB and MO theory see also: L. Pauling and E. B. Wilson, Jr., Introduction to Quantummechanics, McGraw-Hill Book Company Inc., New York 1935. — H. Preuss, Die Methoden der Molekulphysik und ihre Anwendungsbereiche, Fortschr. Physik. 1^0 Sonderband, Akademie-Verlag, Berlin 1959. — J. C. Slater, Quantum Theory of Molecules and Solids, Vol. I McGraw-Hill Book Company Inc., New York 1963.