

The Applicability of Point-Charge Approximations to the Calculation of Molecular Expectation Values

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The recently developed self-consistent charge X α (SCC—X α) method has been utilised to investigate various types of point-charge approximations to molecular expectation values. In the first part observables of the structure $m_l(r) r^l \hat{Y}_L(r)$ and $a_l(r) r^{l-1} \hat{Y}_L(r)$, respectively, are analysed yielding the conclusion that, in general, only certain matrix elements can be treated by point-charge approximations, namely the two-center crystal-field integrals and the three-center integrals. The results are then applied to the calculation of the total valence energies as a function of bond distances, and it turns out that the SCC—X α method is able to reproduce equilibrium geometries with deviations of less than 10% provided all matrix elements are evaluated in an exact way, while all investigated types of point-charge approximations fail in predicting geometries.

I. INTRODUCTION

It is sometimes claimed with a slightly disapproving attitude that all problems in (nonrelativistic) quantum chemistry are solved at least principally because the solution of the N-particle Schrödinger equation is merely a technical problem. This statement is, I think, basically incorrect. For, the scope of the theoretical development cannot exhaust itself in the implementation of a formal calculus. On one hand, it has to establish the connection between the established experimental and theoretical knowledge. On the other hand, the applications of a theory are not only illustrative but are essential for the demonstration of its efficiency and, thus, for its acceptance within the scientific community. Therefore, quantum chemistry is far from being simply a straightforward application of quantum mechanics to chemical bonding. It also has to develop special methods to describe the relevant experimental facts and to interpret the common more phenomenological theoretical concepts of chemistry such as electronegativity, basicity, acidity, and others.

To this field of research, the so-called *ab initio* methods have contributed comparatively little so far, because their problems are naturally determined by mainly internal theoretical interests and their acceptance results from the sound theoretical basis but not from their applicability to actual problems. There is consequently an inevitable need for simpler, *i. e.* semiempirical molecular-orbital methods not only for the practical reason of applicability, as com-

monly supposed, but also as the necessary link between exact and phenomenological theoretical concepts. Thus, a criterion for the quality of a semiempirical MO-method should be among others, its ability to give a reasonable description of observable quantities or to reproduce experimental data in terms of simple and familiar theoretical concepts.

It may now happen that the calculation of such observables may exceed by far the computation time for the MO-calculation itself. It is, therefore, desirable to know to which extent approximations are possible in the evaluation of the respective expectation values. This will be analysed here for two types of observables which are representative in the sense that many of the actual experimental quantities can be subsumed under them, namely the multipole moments and the inverse multipole moments, *i. e.* the $\langle r^P \rangle$ expectation values. Moreover, they can serve as a measure for the quality of the molecular charge density $\rho(\vec{r})$, since they are affected already by first-order changes in the wave functions unlike the energies. The semiempirical MO-method constituting the basis of our investigations is the recently developed self-consistent-charge- $X\alpha$ (SCC- $X\alpha$) method¹ which is the combination of some basic ideas of the iterative extended Hückel method² and the $X\alpha$ -approximation³. It has already shown its ability for the interpretation of spectral data in several cases.

The scope of this contribution will be thus as follows. In the second part we will give a concise description of the underlying physical concepts of the SCC- $X\alpha$ method, while in the third, the general structure of the expectation values and the evaluation of the corresponding matrix elements will be derived. Then follows a comparison and discussion of the numerical results for the matrix elements under various approximations and, finally, we will treat, as an application, the calculation of total energies and geometries in the frame of the SCC- $X\alpha$ method.

II. THEORY

The SCC- $X\alpha$ method¹ starts from an LCAO-one-electron Hamiltonian separated into an atomic part and the neighbour contributions to the potential according to

$$H_{ij}^{\mu\nu} = [(\varepsilon_i^\mu + \varepsilon_j^\nu) S_{ij}^{\mu\nu} + (V_{ij}^{\mu\nu} + V_{ji}^{\nu\mu})]/2 \quad (1)$$

ε_i^μ is the negative of the atomic ionisation potential of orbital i centered at the μ -th atom, $S_{ij}^{\mu\nu}$ is the overlap matrix, and the potential matrix elements are defined as

$$V_{ij}^{\mu\nu} = \sum_{\alpha \neq \nu} \int \phi_i^{(\mu)}(\vec{r} - \vec{R}_{i\mu}) V_{\alpha i}^{(\alpha)}(\vec{r} - \vec{R}_{\alpha\nu}) \phi_j^{(\nu)}(\vec{r}) d^3r \quad (2)$$

with respect to some appropriate atomic basis functions $\phi_i^{(\mu)}(\vec{r})$ chosen here for simplicity as Slater-type orbitals (STO). The simplest MO-method founded on such a formulation as Eq. (1) is the Wolfsberg-Helmholtz or extended Hückel method⁴, which can be deduced from Eq. (1) according to the virial theorem by the additional simplification

$$V_{ij}^{\mu\nu} + V_{ji}^{\nu\mu} = k_{ij}' (1 - \delta_{ij}) (\varepsilon_i^\mu + \varepsilon_j^\nu) S_{ij}^{\mu\nu}$$

yielding the well-known WH-Hamiltonian

$$H_{ij}^{\mu\nu} = k_{ij} (\varepsilon_i^\mu + \varepsilon_j^\nu) S_{ij}^{\mu\nu}/2 \quad (3)$$

containing the molecule-dependent parameters $k_{ij} = 1 + k_{ij}'(1 - \delta_{ij})$ and ε_i^μ , *i. e.* their values have to be adjusted principally according to the molecule under consideration. Thus, the WH-method is mainly empirical and although it may serve as a first tool for the energy spectrum and the eigenvectors, it is in general of limited value for the interpretation of any spectral quantities.

Furthermore, the eigenvalues of the WH-Hamiltonian are not invariant against a translation of the energy scale unless k_{ij} equals unity. It can be asked, therefore, if the WH-method allows an extension to a theory based on a universal, *i. e.* molecule-independent parameter set. To this end two effects have to be taken into account, namely:

1. An atom in a molecule generally does not behave as a neutral but as a charged species. Since ε_i^μ is charge dependent, charge corrected values have to be used instead of free atomic ionisation potentials. This may be seen as an atomic-type effect.
2. The neighbour contributions to the potential at an atomic site are in general considerably smaller than the respective atomic quantities. However, their importance arises from that the molecular symmetry predominantly enters via the potential matrix elements. This will be called the molecular effect.

By incorporating the atomic effect one obtains the iterative extended Hückel theory², which is a self-consistent-charge method because the Hamiltonian is charge dependent via ε_j^ν . Although this modification yields considerably improved results it does not describe correctly *e. g.* the differences in σ - and π -interactions in a universal parameter set. This can be achieved only when including the neighbour contributions to the potential explicitly, as well. In doing so, one has to search for a reasonable but sufficiently simple potential allowing the fast calculation of the matrix elements, Eq. (2). This requirement can be fulfilled in representing the potential as a local functional of the elec-

tronic density $\rho(r)$, especially in the $X\alpha$ -approximation³. Furthermore, from observing that $\ln \rho(r)$ is an almost linear function of r in the outer region (cf. Figure 1), where the chemical bond takes place, the atomic charge density $\rho_{at}(r)$ is assumed to be proportional to $\exp(-\eta r)$ yielding in atomic Ry-units¹

$$V_{at}(r) = -2(Q + N e^{-\eta r})/r - \eta e^{-\eta r} (N + \alpha' N^{1/3}) \quad (4)$$

Here, N describes the number of electrons, $Q = Z - N$ is the effective atomic charge, the exchange parameter α' is taken to be equal to 0.706 for all atoms,^{1,5} and the approximation (4) provides that the valence electrons can be treated separately from the core electrons (strict core-valence separability). The potential parameter η has an evident interpretation. For hydrogen, the atomic wave function is a single exponential likewise, $\phi \sim \exp(-\zeta r)$, and we have thus $\eta = 2\zeta$; for heavier atoms, η can be determined *e. g.* from the slope of $\rho_{at}(r)$ with respect to r . Owing to the well-known charge and configuration dependency of the orbital exponents ζ ⁶, the potential parameter has been chosen as

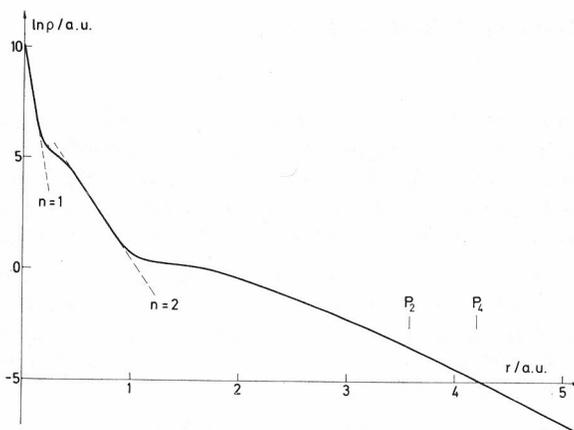


Figure 1. — The logarithm of the electronic density of the neutral phosphorus atom as obtained from double-zeta basis functions. Also shown are the bond distances of P_2 and P_4 .

charge dependent, too. Consequently, the SCC— $X\alpha$ method contains three types of parameters all assumed to be charge dependent, namely

$$\left. \begin{array}{ll} \text{atomic ionisation potentials} & \varepsilon_j^\nu = \varepsilon_{j0}^\nu + \varepsilon_{j1}^\nu Q_\nu + \varepsilon_{j2}^\nu Q_\nu^2 \\ \text{atomic orbital exponents} & \zeta_j^\nu = \zeta_{j0}^\nu + \zeta_{j1}^\nu Q_\nu \\ \text{atomic potential parameter} & \eta_\nu = \eta_{\nu 0} + \eta_{\nu 1} Q_\nu \end{array} \right\} \quad (5)$$

As has been described earlier⁷, ε_{j1}^ν , ε_{j2}^ν , ζ_{j0}^ν , ζ_{j1}^ν , and $\eta_{\nu 1}$ are determined from atomic data whereas $\eta_{\nu 0}$ and ε_{j0}^ν are fitted to molecular ionisation potentials and dipole moments of some small reference molecules. Furthermore, the atomic modelpotential of Eq. (4) is obtained as a function of the effective charge of the respective atom via N , Q , η making a self-consistent charge iteration procedure applicable in a natural way. Additionally, its simple form allows the calculation of all three-center integrals exactly from a single-center expansion into partial waves¹.

In conclusion, the SCC— $X\alpha$ method fulfills the requirements of a semi-empirical MO-method mentioned in the introduction in so far, as the number of free fit-parameters has been kept small, namely three per main-group element, and moreover these parameters allow an interpretation in simple and familiar concepts. This feature is unlike many of the neglect-of-differential-overlap methods where one meets a lot of parameters without a clear physical significance resulting sometimes in degeneration to a pure fit-procedure in order to reproduce a certain class of physical observables. Furthermore, the SCC— $X\alpha$ method has been successfully applied to the interpretation of photoelectron spectra⁷⁻⁹, Mößbauer spectra^{10,11}, ESCA chemical shifts¹¹, and to the calculation of total energies^{7,12}. Finally, it should be mentioned that as a result of these applications on about 250 molecules the parameter set (5) turns out to be universal, *i. e.* it depends on the atoms only and not on the specific mo-

lecular bonding situation. A further advantage of the SCC— $X\alpha$ method is its simple feasibility, the equally good applicability to systems containing heavier atoms, its stable convergence properties even in larger systems, and a computation time exceeding that of an iterative extended Hückel method by a factor of approximately only three per iteration step.

III. EXPECTATION VALUES

The general expression for the electronic part of the expectation value of a molecular observable A is

$$\langle A \rangle_{\text{el}} = \langle \Psi | A | \Psi \rangle \quad (6)$$

where $\Psi = \Psi(\vec{r}_1, \dots, \vec{r}_n)$ is the molecular many-particle wave function usually approximated by a linear combination of Slater determinants. In the special case, A being a single-particle operator, the Slater determinant yields the same result as an unsymmetrised Hartree product, namely

$$\langle A \rangle_{\text{el}} = \sum_k n_k \langle \psi_k | A | \psi_k \rangle \quad (7)$$

with the molecular orbitals $\psi_k(\vec{r})$ and the respective occupation numbers n_k . In an LCAO basis

$$\psi_k(\vec{r}) = \sum_{vj} c_{jk}^v \phi_j^{(v)}(\vec{r} - \vec{R}_v), \quad (8)$$

the standard expression for the electronic part of A is obtained as

$$\langle A \rangle_{\text{el}} = \text{tr}(PA) = \sum P_{ij}^{v'v} A_{ij}^{v'v}. \quad (9)$$

The $A_{ij}^{v'v}$ are the matrix elements of A with respect to the AO-basis,

$$A_{ij}^{v'v} = \int \phi_i^{(v')}(\vec{r} - \vec{R}_{v'}) A(\vec{r} - \vec{R}_{v'}) \phi_j^{(v)}(\vec{r} - \vec{R}_v) d^3r, \quad (10)$$

and it should be kept in mind that in general $A_{ij}^{v'v}$ will depend on R_0 which will be omitted for convenience. The results of the MO-calculation enter $\langle A \rangle_{\text{el}}$ via the first order density or bond order matrix

$$P_{ij}^{v'v} = \sum_k n_k c_{ik}^{v'} c_{jk}^v. \quad (11)$$

In terms of the $P_{ij}^{v'v}$ the net charges and the overlap charges are immediately obtained as¹³

$$N^{vv} = \sum_{ij} P_{ij}^{vv} S_{ij}^{vv} \quad (12)$$

and

$$N^{v'v} = 2 \sum_{ij} P_{ij}^{v'v} S_{ij}^{v'v}, \quad (13)$$

respectively.

In evaluating the $A_{ij}^{v'v}$ we will distinguish among three types of point charge approximations:

1. The weakest one we shall denote as core-pca, meaning that only the core electrons and core densities are substituted by δ -functions, *i. e.* the core is treated as a point charge while all the other contributions from the valence electrons are taken into account exactly. This approximation is inherent in most of the valence-electron-only MO-methods.

2. The next stage of simplification is the bond-pca, where the valence density is split into atomic-site and bond-site point charges $N^{\nu\nu}$ and $N^{\nu'\nu}$, respectively. It should be displayed that no scheme of population analysis will enter the calculation of $\langle A \rangle$ because the overlap charge $N^{\nu'\nu}$ is not distributed between atoms ν and ν' .

3. Finally, the strongest simplification is the valence-pca treating also the valence electrons as point charges, *i. e.* $N^{\nu\nu}$ and $N^{\nu'\nu}$ are replaced with a population analysis dependent effective number N_ν of electrons which is *e. g.* according to Mulliken¹³

$$N_\nu = \sum_{\nu'} N^{\nu'\nu}$$

In this approximation the molecule is thus described as a collection of point charges $Q_\nu = Z_\nu - N_\nu$.

The core-pca is used throughout this paper. Its validity for most purposes can be checked easily within the frame of the SCC— $X\alpha$ approximation in a natural way, especially for the computation of expectation values as has been demonstrated earlier¹¹. Under this assumption $\langle A \rangle$ can be written with respect to the site \vec{R}_0 as

$$\langle A \rangle = \sum_{\nu} Z_\nu^{co} A(\vec{R}_{\nu 0}) - \sum_{\nu'\nu} \sum_{ij} P_{ij}^{\nu'\nu} A_{ij}^{\nu'\nu} \quad (14)$$

where now $Z_\nu^{co} = Z_\nu - N_\nu^{co}$ is the core charge of the ν -th atom and $\vec{R}_{\nu 0} = \vec{R}_\nu - \vec{R}_0$. Furthermore, we restrict ourselves here to position dependent observables because momentum dependent ones can be treated in a similar fashion using the Fourier transforms of the wave functions $\phi_i^{(\nu)}(\vec{r})$. In the general case four types of integrals will occur evaluated by different strategies:

1. One-center integrals, *i. e.* $\vec{R}_\nu = \vec{R}_{\nu'} = \vec{R}_0$:

$$A_{ij}^{00} = \int \phi_i^{(0)}(\vec{r}) A(\vec{r}) \phi_j^{(0)}(\vec{r}) d^3r \quad (15)$$

These integrals are not computed in that atomic basis set used for the MO calculation and normally consisting of one or two STO's, but are determined over a (possibly relativistic) accurate atomic calculation as a function of the various charges and configurations, *i. e.*

$$A_{ij}^{00} = A_{ij}^{atom}(x_{ns}^0, x_{np}^0, x_{nd}^0, \dots)$$

Therefore, the MO results enter the A_{ij}^{00} only via the occupation numbers x_{nl}^0 of the valence shell.

2. Resonance integrals, *i. e.* $\vec{R}_\nu \neq \vec{R}_{\nu'}$ and $\vec{R}_{\nu'} = \vec{R}_0$ or $R_\nu = R_0$:

$$A_{ij}^{0\nu} = \int \phi_i^{(0)}(\vec{r}) A(\vec{r}) \phi_j^{(\nu)}(\vec{r} - \vec{R}_{\nu 0}) d^3r \tag{16}$$

Although principally depending on the explicit structure of $A(\vec{r})$ it is, on the one hand, our experience from dipole moment as well as electric field gradient calculations, that these integrals have to be computed exactly while, on the other, in case of second moments and $1/r$ -expectation values, point charge approximations are sufficiently accurate.

3. Crystal-field integrals, *i. e.* $\vec{R}_\nu = \vec{R}_{\nu'} \neq \vec{R}_0$:

$$A_{ij}^{\nu\nu} = \int \phi_i^{(\nu)}(\vec{r}) A(\vec{r} + \vec{R}_{\nu 0}) \phi_j^{(\nu)}(\vec{r}) d^3r \tag{17}$$

These integrals are evaluated by using a partial wave expansion of $A(\vec{r} + \vec{R})$ symbolically written as

$$A(\vec{r} + \vec{R}) = 4\pi \sum_{lm} \alpha_l(r, R) Y_{lm}^*(\hat{R}) \hat{Y}_{lm}(\hat{r}) \tag{18}$$

with some radial part $\alpha_l(r, R)$. The first term of this expansion again leads to an atomic-type expectation value while the higher order terms will give an estimate for the reliability of point charge approximations as we will see later.

4. Three-center integrals, *i. e.* $\vec{R}_\nu, \vec{R}_{\nu'}, \vec{R}_0$ are pairwise different:

$$A_{ij}^{\nu'\nu} = \int \phi_i^{(\nu')}(\vec{r} - \vec{R}_{\nu' 0}) A(\vec{r} + \vec{R}_{\nu 0}) \phi_j^{(\nu)}(\vec{r}) d^3r \tag{19}$$

Using the same expansion, Eq. (18), the first (spherical) term has the structure of a resonance integral while higher order terms can be estimated by a Mulliken approximation

$$\phi_i^{(\nu')}(\vec{r} - \vec{R}_{\nu' 0}) = \sum_{k \in \nu} S_{ik}^{\nu'\nu} \phi_k^{(\nu)}(\vec{r}) \tag{20}$$

for the wave function displaced from the origin.

In the bond-pca, meaning that the overlap charge $N^{\nu'\nu}$ will be placed at the center of $\vec{R}_{\nu' 0}$, the exact expression for $\langle A \rangle$, Eq. (14), is transformed to

$$\begin{aligned} \langle A \rangle_{\text{bpca}} = & \sum_{\nu \neq 0} (Z_\nu^{co} - N^{\nu\nu}) A(\vec{R}_{\nu 0}) - \sum_{ij} P_{ij}^{00} A_{ij}^{00} \\ & - 2 \sum_{\nu \neq 0} N^{0\nu} A(\vec{R}_{\nu 0}/2) - \sum'_{\nu'\nu} N^{\nu'\nu} A((\vec{R}_{\nu 0} + \vec{R}_{\nu' 0})/2) \end{aligned} \tag{21}$$

while in valence-pca we obtain

$$\langle A \rangle_{\text{vpca}} = \sum_{\nu \neq 0} Q_\nu A(\vec{R}_{\nu 0}) - \sum_i x_i^0 A_{ii}^{00} - \sum'_{ij} P_{ij}^{00} A_{ij}^{00} \tag{22}$$

In what follows we will compare these various approximations with each other for two types of observables, namely the multipole moments and the inverse multipole moments

$$\vec{M}_L(r) = m_l(r) r^l \hat{Y}_L(r) \quad (23)$$

$$A_L(r) = a_l(r) r^{-l-1} \hat{Y}_L(r) \quad (24)$$

where $m_l(r)$ and $a_l(r)$ are functions not depending on angular variables and L is a short-hand notation for (lm) . From Eq. (23) we obtain, *e. g.*, with $m_l \equiv 1$ the charge density as $\vec{M}_{00}(r)$, the dipole moment components as $M_{1m}(r)$, and the second moments $M_{2m}(r)$, while $A_{00}(r)$ is proportional to the electrostatic potential at a nucleus, and the electric field gradient tensor components are derived from Eq. (24) for $l = 2$ and $a_2(r) = 1 - \gamma(r)$ where $\gamma(r)$ is the Sternheimer shielding factor¹⁰.

Let us turn first to $M_L(r)$ for the special case $m_l(r)$ being a constant. Then all three-center integrals can be reduced to two-center integrals yielding *e. g.* for the electronic contribution to the dipole moment

$$\begin{aligned} \vec{M}_{ij}^{00} &= \vec{r}_{ij}^{00}; & \vec{M}_{ij}^{0\nu} &= \vec{R}_{\nu 0} \vec{S}_{ij}^{0\nu}/2 + \vec{r}_{ij}^{0\nu} \\ \vec{M}_{ij}^{\nu\nu} &= \vec{R}_{\nu 0} \vec{S}_{ij}^{\nu\nu} + \vec{r}_{ij}^{\nu\nu}; & \vec{M}_{ij}^{\nu'\nu} &= (\vec{R}_{\nu 0} + \vec{R}_{\nu 0'}) \vec{S}_{ij}^{\nu'\nu}/2 + \vec{r}_{ij}^{\nu'\nu} \end{aligned}$$

which may be cast into the compact form

$$\vec{M}_{ij}^{\nu'\nu} = (\vec{R}_{\nu'} + \vec{R}_{\nu}) \vec{S}_{ij}^{\nu'\nu}/2 + \vec{r}_{ij}^{\nu'\nu} \quad (25)$$

where the translational invariance has been used and

$$\vec{r}_{ij}^{\nu'\nu} = \int \phi_i^{(\nu')}(\vec{r} + \vec{R}_{\nu\nu}/2) \vec{r} \phi_j^{(\nu)}(\vec{r} - \vec{R}_{\nu\nu}/2) d^3r \quad (26)$$

is easily calculated by the Fourier transformation method¹⁴. The dipole moment can thus be presented in the form

$$\vec{\mu} = \vec{\mu}_Q + \vec{\mu}_H + \vec{\mu}_R \quad (27)$$

$$\vec{\mu}_Q = \sum_{\nu} (Z_{\nu} e_0 - N^{\nu\nu}) \vec{R}_{\nu} - \sum'_{\nu\nu'} (\vec{R}_{\nu'} + \vec{R}_{\nu}) N^{\nu\nu'} \quad (28)$$

$$\vec{\mu}_H = - \sum_{vij} P_{ij}^{\nu\nu} \vec{r}_{ij}^{\nu\nu} \quad (29)$$

$$\vec{\mu}_R = - \sum'_{\nu\nu'} \sum_{ij} P_{ij}^{\nu'\nu} \vec{r}_{ij}^{\nu'\nu} \quad (30)$$

where $\vec{\mu}_Q$ stands for the point charge contribution, $\vec{\mu}_H$ is the hybridisation term, which explicitly contributes to only the integrals with $i \neq j$ since \vec{r}_{ii} equals zero due to the vector coupling selection rules.

In order to calculate the second moments let us introduce first the dyadic product of two vectors as the matrix with the components

$$\langle \vec{a}; \vec{b} \rangle_{\alpha\beta} = a_\alpha b_\beta; \quad \alpha, \beta = x, y, z \quad (31)$$

The second moment tensor of a molecule at the center of mass or any atomic site \vec{R}_0 can be brought then into the form

$$\vec{\tau} = \sum_{\nu} Z_{\nu} e_0 \langle \vec{R}_{\nu 0}; \vec{R}_{\nu 0} \rangle - \sum_{\nu\nu'} P_{ij}^{\nu\nu'} \vec{T}_{ij}^{\nu\nu'} \quad (32)$$

where

$$\begin{aligned} \vec{T}_{ij}^{\nu\nu'} &= \int \phi_i^{(\nu)}(\vec{r} - \vec{R}_{\nu 0}) \langle \vec{r}; \vec{r} \rangle \phi_j^{(\nu')}(\vec{r} - \vec{R}_{\nu 0}) d^3r \\ &= \langle \vec{R}_{\nu 0}; \vec{M}_{ij}^{\nu\nu'} \rangle + \langle \vec{M}_{ij}^{\nu\nu'}; \vec{R}_{\nu 0} \rangle - \langle \vec{R}_{\nu 0}; \vec{R}_{\nu 0} \rangle S_{ij}^{\nu\nu'} + \langle \vec{r}; \vec{r} \rangle_{ij}^{\nu\nu'} \end{aligned} \quad (33)$$

$$\langle \vec{r}; \vec{r} \rangle_{ij}^{\nu\nu'} = \int \phi_i^{(\nu)}(\vec{r} - \vec{R}_{\nu 0}) \langle \vec{r} - \vec{R}_{\nu 0}; \vec{r} - \vec{R}_{\nu 0} \rangle \phi_j^{(\nu')}(\vec{r} - \vec{R}_{\nu 0}) d^3r \quad (34)$$

The last term can be evaluated again easily by the Fourier transformation method. Substituting now $\vec{M}_{ij}^{\nu\nu'}$ with Eq. (25) the second moment tensor may be cast into a form analogous to Eq. (27)

$$\vec{\tau} = \vec{\tau}_Q + \vec{\tau}_D + \vec{\tau}_H + \vec{\tau}_R \quad (35)$$

$$\vec{\tau}_Q = \sum_{\nu} (Z_{\nu} e_0 - N^{\nu\nu}) \langle \vec{R}_{\nu 0}; \vec{R}_{\nu 0} \rangle - \frac{1}{2} \sum_{\nu\nu'} (\langle \vec{R}_{\nu 0}; \vec{R}_{\nu 0} \rangle + \langle \vec{R}_{\nu' 0}; \vec{R}_{\nu' 0} \rangle) N^{\nu\nu'} \quad (36)$$

$$\vec{\tau}_D = - \sum_{\nu\nu'} (\langle \vec{R}_{\nu 0}; \vec{r}^{\nu\nu'} \rangle + \langle \vec{r}^{\nu\nu'}; \vec{R}_{\nu 0} \rangle) \quad (37)$$

$$\vec{\tau}_H = - \sum_{\nu ij} P_{ij}^{\nu\nu'} \langle \vec{r}; \vec{r} \rangle_{ij}^{\nu\nu'} \quad (38)$$

$$\vec{\tau}_R = - \sum_{\nu\nu'} \sum_{ij} P_{ij}^{\nu\nu'} \langle \vec{r}; \vec{r} \rangle_{ij}^{\nu\nu'} \quad (39)$$

where in Eq. (37) the abbreviation has been used

$$\vec{r}^{\nu\nu'} = \sum_{ij} P_{ij}^{\nu\nu'} \vec{r}_{ij}^{\nu\nu'} \quad (40)$$

Unlike $\vec{\mu}_H$, Eq. (29), the tensor $\vec{\tau}_H$ also contains the terms $i = j$ and is thus not a hybridisation term in a strict sense.

Although Eqs. (35)–(39) look a little cumbersome at first sight, this splitting has the advantage in that $\vec{\tau}_H$ as well as the most complicated term $\vec{\tau}_R$ is invariant against the choice of the origin and, moreover, $\vec{\tau}_R$ will turn out to be almost negligible compared with the other contributions justifying an approximate treatment altogether.

Unlike the multipole moments the matrix elements of $A_L(\vec{r})$ cannot be reduced to two-center integrals without any additional approximations even when $a_l(r)$ is assumed to be constant. Furthermore, some of the one-center integrals

$$A_{ij,L}^{00} = \int \phi_i^{(0)}(\vec{r}) A_L(\vec{r}) \phi_j^{(0)}(\vec{r}) d^3r = G_L(L_i L_j) \langle a_l(r) r^{l-1} \rangle_{ij} \quad (41)$$

with the Gaunt numbers $G_L(L_i L_j)$ can diverge unless $a_l(r) \sim r^\lambda$, $\lambda \geq l-1$, for r approaching zero. The same may hold for the resonance integrals

$$A_{ij,L}^{0\nu} = \int \phi_i^{(0)}(\vec{r}) r^{l-1} a_l(r) Y_L(\hat{r}) \phi_j^{(\nu)}(\vec{r} - \vec{R}_{\nu 0}) d^3r \quad (42)$$

requiring in general a numerical integration of the radial part of this integral. On the other hand, one is not faced with these problems in evaluating the crystal-field and the three-center integrals where we apply the expansion formula for the irregular spherical harmonics¹⁵

$$|\vec{r} + \vec{R}|^{-1} Y_L(\widehat{\vec{r} + \vec{R}}) = \sum_{\Lambda} \Gamma_{\Lambda}(L) r_{<}^{\lambda} Y_{\Lambda}^*(r_{<}) r_{>}^{-(l+\lambda+1)} \hat{Y}_{L+\Lambda}(r_{>}) \quad (43)$$

$$\Gamma_{\Lambda}(L) = (-1)^{\lambda} \sqrt{\frac{4\pi}{2\lambda+1} \frac{2l+1}{2(l+\lambda+1)} \frac{(l+\lambda-(m+\mu))!(l+\lambda+m+\mu)!}{(l+m)!(l-m)!(\lambda+\mu)!(\lambda-\mu)!}}$$

and assume that $a_l(|\vec{r} + \vec{R}|)$ can be replaced with an average \bar{a}_l in the vicinity of \vec{R} . The justification for this approximation can be proven in any concrete case on the basis of an analogous partial wave expansion, Eq. (18), for $a_l(|\vec{r} + \vec{R}|)$ by comparing the first term with the higher aspherical terms of this expansion. Moreover, as we will demonstrate in the next section, Eq. (43) may be restricted to the region where $r < R$, yielding as the final result from Eqs. (17) and (19)

$$A_{ij,L}^{\nu\nu} = \sum \Gamma_{\Lambda}(L) R_{\nu 0}^{-(l+\lambda+1)} Y_{L+\Lambda}(\hat{R}_{\nu 0}) G_{\Lambda}(L_j L_i) \langle r^{\lambda} \rangle_{ij}^{\nu\nu} \quad (44)$$

$$A_{ij,L}^{\nu'\nu} = \sum \Gamma_{\Lambda}(L) \hat{R}_{\nu 0}^{-(l+\lambda+1)} Y_{L+\Lambda}(\hat{R}_{\nu 0}) \int \phi_i^{(\nu')}(\vec{r} - \vec{R}_{\nu' 0}) r^{\lambda} Y_{\Lambda}^*(\hat{r}) \phi_j^{(\nu)}(\vec{r}) d^3r \quad (45)$$

The remaining integral in Eq. (45) is essentially a two-center integral which, however, need not be calculated explicitly as we will see in the next section.

IV. RESULTS

Let us discuss first the dipole moment contributions listed in Table I according to Eqs. (28)–(30). Also given is the total dipole moment together with the corresponding experimental values for comparison. As the most remarkable result, μ_R turns out generally far from being negligible and this may lead to the conclusion that any type of point charge approximation is inappropriate for obtaining reasonable μ -values. However, one could try to

TABLE I
Dipole Moment Components According to Eqs. (28)—(30), Mulliken Approximated Values, Eq. (46), and Total Calculated and Experimental Values

Molecule	μ_Q debye	μ_H debye	μ_R debye	μ_R^{Mull} debye	μ_{tot} debye	μ_{exp} debye
H ₂ O ₂	1.24	1.80	-0.95	-0.24	2.09	2.18
H ₂ O	0.75	2.21	-1.13	-0.28	1.83	1.85
O ₃	0.64	-0.07	0.08	0.09	0.65	0.58
OF ₂	0.46	-0.29	0.03	0.05	0.20	0.3
OCl ₂	1.59	-0.87	0.10	0.02	0.82	
NH ₃	0.27	1.85	-0.63	-0.22	1.49	1.468
PH ₃	-1.42	4.35	-2.18	-0.52	0.75	0.578
AsH ₃	-2.64	5.21	-2.37	-0.52	0.20	0.22
SbH ₃	-3.81	6.16	-2.23	-0.55	0.12	0.116
c-C ₃ H ₄	0.12	0.42	-0.11	-0.09	0.43	0.46
ClF	1.89	-1.09	0.10	0.04	0.90	0.888
IBr	0.82	-0.20	0.21	-0.01	0.83	0.74
ClF ₃	1.66	-1.93	0.80	0.36	0.53	0.56
PF ₃	3.02	-2.04	0.07	0.22	1.05	1.025
PCl ₃	1.23	-0.35	-0.34	0.07	0.54	0.56
PBr ₃	0.08	0.08	-0.01	0.11	0.15	
PI ₃	-0.91	0.84	-0.56	0.06	-0.63	

compute $\vec{\mu}_R$ approximately on the basis of the Mulliken expansion formula, Eq. (20), for one of the wave functions yielding

$$\vec{\mu}_R^{\text{Mull}} = \sum_{\nu k j} \langle \vec{r} \rangle_{k j}^{\nu \nu} \sum_{\nu' i} S_{k i}^{\nu \nu'} P_{i j}^{\nu' \nu} \quad (46)$$

These values are listed in the fourth column of Table I demonstrating that even Eq. (46) is generally not sufficient in describing the resonance contributions μ_R correctly, and yielding even the wrong sign in a few cases. Furthermore, none of the three constituents of $\vec{\mu}$ can be assumed to be dominant through the whole series thus making a careful evaluation of the dipole moment integrals necessary.

The situation changes, however, completely when observing the second moments relative to the center of mass, Eqs. (36)—(39), listed in Table II. Here, $\vec{\tau}_R$ is almost completely negligible while the dominant contribution to $\vec{\tau}$ arises from $\vec{\tau}_H$. This is valid especially for one- or two-dimensional molecules where the out-of-plane value is determined by $\vec{\tau}_H$ only since the respective $\vec{\tau}_Q$ and $\vec{\tau}_D$ vanish in these systems. It is therefore of central importance to determine the one-center contributions from exact atomic expectation values in combination with charges and occupation numbers as obtained from an MO-calculation, while two-center terms may be treated only as approximative, or can even be neglected as can be gathered from the fifth and sixth columns of Table II.

This result is in complete accordance with the thorough investigations of Maksić and co-workers on second moments¹⁶ resulting in their well-known additivity rules for the electronic second moments. It is hardly necessary to repeat their findings here.

TABLE II
Second Moment Contributions According to Eqs. (36)—(39) and Electronic Contributions

Molecule	τ_O	τ_D	τ_H	τ_R	Electronic part		
	a. u.	a. u.	a. u.	a. u.	One-center	Total	
H_2O_2 $\langle x^2 \rangle$	0.43	-0.45	-9.63	-0.034	-10.52	-11.52	
	$\langle y^2 \rangle$	1.06	-0.88	-9.08	0.000	-10.95	-13.28
	$\langle z^2 \rangle$	0.21	-2.78	-7.93	0.004	-34.61	-38.57
	$\langle yz \rangle$	-1.10	-0.56	-0.28	0.002	0.15	2.62
H_2O $\langle x^2 \rangle$	0.25	-0.60	-5.26	-0.022	-6.58	-7.65	
	$\langle y^2 \rangle$	0.54	-0.97	-4.54	-0.002	-6.69	-9.06
	$\langle z^2 \rangle$	0.	0.	-5.87	-0.060	-5.87	-5.93
O_3 $\langle x^2 \rangle$	-0.11	-1.86	-11.20	0.025	-18.82	-19.34	
	$\langle y^2 \rangle$	-0.85	-4.63	-9.70	0.073	-63.84	-65.89
	$\langle z^2 \rangle$	0.	0.	-10.28	-0.063	-10.28	-10.34
OCl_2 $\langle x^2 \rangle$	-0.72	-2.69	-19.96	0.052	-37.19	-38.15	
	$\langle y^2 \rangle$	2.41	-6.66	-18.11	0.073	-118.27	-120.31
	$\langle z^2 \rangle$	0.	0.	-21.96	-0.019	-21.96	-21.98
NH_3 $\langle x^2 \rangle$	0.23	-1.30	-5.32	-0.058	-8.05	-11.15	
	$\langle z^2 \rangle$	0.05	-0.30	-7.01	-0.102	-7.87	-8.50
SbH_3 $\langle x^2 \rangle$	-2.95	-1.82	-11.02	-0.033	-21.56	-26.48	
	$\langle z^2 \rangle$	-2.58	-1.72	-12.77	-0.039	-22.21	-26.44
$c-C_3H_4$ $\langle x^2 \rangle$	0.30	-6.45	-12.62	-0.050	-31.08	-48.62	
	$\langle y^2 \rangle$	-0.14	-1.46	-12.28	-0.397	-16.38	-20.26
	$\langle z^2 \rangle$	-0.07	-6.55	-12.43	-0.112	-38.61	-59.93
ClF $\langle x^2 \rangle$	0.	0.	-12.35	-0.007	-12.35	-12.36	
	$\langle z^2 \rangle$	-0.68	-4.04	-9.59	0.083	-49.37	-50.27
IBr $\langle x^2 \rangle$	0.	0.	-27.44	-0.035	-27.44	-27.48	
	$\langle z^2 \rangle$	-0.35	-8.59	-21.48	0.193	-108.04	-110.59
N_2 $\langle x^2 \rangle$	0.	0.	-6.11	-0.140	-6.11	-6.25	
	$\langle z^2 \rangle$	0.	-4.62	-7.62	0.079	-20.95	-22.88
As_2 $\langle x^2 \rangle$	0.	0.	-17.44	-0.270	-17.44	-17.70	
	$\langle z^2 \rangle$	0.	-13.93	-19.47	0.358	-66.15	-72.05
ClF_3 $\langle x^2 \rangle$	-0.82	-2.97	-17.26	0.043	-66.47	-66.63	
	$\langle y^2 \rangle$	-6.73	-3.73	-16.37	0.042	-169.99	-170.66
	$\langle z^2 \rangle$	0.	0.	-19.18	0.001	-19.18	-19.18
PF_3 $\langle x^2 \rangle$	-2.60	-3.74	-15.85	0.025	-87.86	-90.57	
	$\langle z^2 \rangle$	0.52	-4.61	-17.81	0.048	-31.30	-32.24
PI_3 $\langle x^2 \rangle$	1.48	-11.34	-51.17	0.076	-237.62	-242.40	
	$\langle z^2 \rangle$	-0.63	-6.39	-54.97	0.046	-77.34	-80.98

In conclusion, having in mind that a point charge description of the charge density $M_{00}(\vec{r})$ is completely inappropriate leading namely to an unstable system, we can state that with increasing multipole order, the one-center contributions become dominant and thus point charge approximations for the two-center terms become increasingly applicable.

In turning next to the inverse moments, we want to discuss $A_{00}(\vec{r})$ in more detail, firstly, because of its importance *e. g.* for the calculation of ESCA shifts and total energies and, secondly, because most of the results are equally valid for the higher inverse moments. Starting with the crystal-field integrals

$$A_{ij,00}^{\nu\nu} = \sqrt{4\pi} \sum_{\Lambda} (2\lambda + 1)^{-1} G_{\Lambda}(L_i L_j) Y_{\Lambda}^*(\hat{R}_{\nu 0}) \left\langle \frac{r^{\lambda}}{r^{\lambda+1}} \right\rangle_{ij}^{\nu\nu} \quad (47)$$

we will first investigate the radial part

$$\begin{aligned} \left\langle \frac{r^{\lambda}}{r^{\lambda+1}} \right\rangle_{ij}^{\nu\nu} &= R_{0\nu}^{-\lambda-1} \int_0^{R_{\nu 0}} r^{\lambda+2} R_i^{(\nu)}(r) R_j^{(\nu)}(r) dr + R_{\nu 0}^{\lambda} \int_{R_{\nu 0}}^{\infty} r^{-\lambda+1} R_i^{(\nu)}(r) R_j^{(\nu)}(r) dr \\ &= R_{\nu 0}^{-\lambda-1} \int_0^{\infty} r^{\lambda+2} R_i^{(\nu)}(r) R_j^{(\nu)}(r) dr - C_{\lambda} \end{aligned} \quad (48)$$

Under the assumption of $R_i(r)$ being an STO

$$R_i(r) = c_i r^{n_i-1} e^{-\zeta_i r}$$

the correction term C_{λ}

$$C_{\lambda} = c_i c_j R_{\nu 0}^{n_i+n_j} [A_{n_i+n_j+\lambda}(\zeta_{ij} R_{\nu 0}) - A_{n_i+n_j-\lambda-1}(\zeta_{ij} R_{\nu 0})] \quad (49)$$

where $\zeta_{ij} = \zeta_i + \zeta_j$, is reducible to the simple integrals

$$A_n(\zeta R) = R^{-n-1} \int_R^{\infty} r^n e^{-\zeta r} dr \quad (50)$$

obeying the recurrence relation

$$A_n(x) = x^{-1} (n A_{n-1}(x) + e^{-x}) \quad (51)$$

As displayed in the fourth column of Table III, the two integrals in the square brackets of Eq. (49) cancel almost exactly and $A_{ij}^{\nu\nu}$ can be simplified therefore to

$$A_{ij,00}^{\nu\nu} = \sqrt{4\pi} \sum_{\Lambda} (2\lambda + 1)^{-1} G_{\Lambda}(L_i L_j) R_{\nu 0}^{-\lambda-1} Y_{\Lambda}^*(\hat{R}_{\nu 0}) \langle r^{\lambda} \rangle_{ij}^{\nu\nu} \quad (52)$$

This expression we will compare with the point-charge approximation to the crystal-field integral, Eq. (17), which is in this case simply

$$A_{ij,00}^{\nu\nu} = (4\pi)^{-1/2} R_{\nu 0}^{-1} \quad (53)$$

corresponding only to the first term of the partial wave expansion, Eq. (52). Thus, the point charge approximation will be justified to the same extent as

TABLE III
Contributions to the First Inverse Moment Expectation Value in *a. u.*

		Crystal-field			Resonance		Three-center		
		$\lambda = 0$	$\lambda = 1$	$\lambda = 2$	C_0	exact	bpca	exact	bpca
H ₂ O*		-0.164	0.	0.	-0.005	-0.30	-0.47	0.011	0.018
H* ₂ O		-0.912	0.043	0.025	-0.025	-0.22	-0.22	-0.096	-0.096
H ₂ O ₂ *		-0.680	0.015	0.008	-0.003	-0.22	-0.30	-0.059	-0.058
H* ₂ O ₂		-1.393	0.056	0.014	-0.023	-0.22	-0.22	-0.096	-0.097
N*H ₃		-0.257	0.	0.	-0.007	-0.44	-0.73	0.018	0.031
NH* ₃		-0.684	0.021	0.016	-0.029	-0.23	-0.23	-0.194	-0.102
P*H ₃		-0.248	0.	0.	-0.002	-0.28	-0.48	0.011	0.017
PH* ₃		-0.480	0.035	0.002	-0.014	-0.17	-0.15	-0.131	-0.136
As*H ₃		-0.263	0.	0.	-0.001	-0.25	-0.42	0.006	0.009
AsH* ₃		-0.446	0.039	0.001	-0.009	-0.16	-0.13	-0.117	-0.121
Sb*H ₃		-0.260	0.	0.	-0.001	-0.19	-0.31	0.002	0.003
SbH* ₃		-0.409	0.035	0.000	-0.004	-0.13	-0.10	-0.088	-0.091
	C ₁	-0.766	0.003	-0.001	-0.018	-0.45	-0.64	-0.259	-0.248
	C ₃	-0.792	-0.003	0.003	-0.014	-0.47	-0.70	-0.228	-0.200
	H ₁	-0.800	0.001	0.004	-0.031	-0.23	-0.24	-0.349	-0.327
	H ₃	-0.815	-0.002	0.006	-0.026	-0.20	-0.21	-0.384	-0.373
O ₃	O _c	-1.358	0.064	0.027	-0.004	-0.29	-0.31	0.010	0.018
	O _t	-0.999	0.028	0.005	-0.001	-0.12	-0.14	-0.061	-0.059
ClF ₃	Cl	-1.948	0.027	0.016	-0.001	-0.10	-0.11	0.016	0.022
	F _{eq}	-1.503	0.041	0.005	-0.001	-0.04	-0.04	-0.021	-0.022
	F _{ax}	-1.306	0.007	0.010	-0.001	-0.01	-0.01	-0.031	-0.031
P*F ₃		-2.015	0.054	0.017	-0.002	-0.26	-0.33	0.016	0.024
PF* ₃		-1.217	0.039	0.003	-0.003	-0.11	-0.10	-0.088	-0.099
P*I ₃		-1.224	0.045	0.030	-0.001	-0.22	-0.22	0.014	0.023
PI* ₃		-0.787	0.018	0.003	0.000	-0.05	-0.06	-0.056	-0.056

the higher terms in the sum can be neglected. This is indeed the case, at least approximately, as can be seen from the second and third column of Table III, where the aspherical contributions do not exceed 10% of the respective spherical term.

The three-center integrals can be analysed along the same line. For $l = 0$ Eq. (45) takes the form

$$A_{ij,00}^{\nu\nu} = \sqrt{4\pi} \sum_{\Lambda} (2\lambda + 1)^{-1} R_{\nu 0}^{-\lambda-1} Y_{\Lambda}(\hat{R}_{0\nu}) \int \phi_i^{(\nu)}(\vec{r} - \vec{R}_{\nu\nu}) r^{\lambda} Y_{\Lambda}^*(\hat{r}) \phi_j^{(\nu)}(\vec{r}) d^3r \quad (54)$$

The first term is simply

$$A_{ij,00}^{\nu\nu} (\lambda = 0) = (4\pi)^{-1/2} R_{0\nu}^{-1} S_{ij}^{\nu\nu} \quad (55)$$

while the higher order terms can be estimated using the Mulliken expansion

$$A_{ij,00}^{\nu\nu} = \sum_{\Lambda > 0} \frac{\sqrt{4\pi}}{(2\lambda + 1)} \cdot \frac{Y_{\Lambda}(\hat{R}_{0\nu})}{R_{0\nu}^{\lambda+1}} \sum_{k \in \nu} S_{ik}^{\nu\nu} \int \phi_k^{(\nu)}(\vec{r}) r^{\lambda} Y_{\Lambda}^*(\hat{r}) \phi_j^{(\nu)}(\vec{r}) d^3r = \sum_{k \in \nu} S_{ik}^{\nu\nu} A_{kj,00}^{\nu\nu} \quad (56)$$

$A_{kj,00}^{\nu\nu}$ is simply the crystal-field integral components for $\lambda > 0$. Therefore, the three-center integrals can be easily computed and the aspherical terms, Eq. (56), are negligible provided the corresponding crystal-field terms are small. This has already been shown. On the other hand, the three-center integrals can be approximated in bond-pca as

$$A_{ij,L}^{\nu\nu} = A_L(\vec{R}_{\nu 0} + \vec{R}_{j0})/2) S_{ij}^{\nu\nu} \quad (57)$$

Although this formula has the drawback that the argument of A_L can vanish and therefore some caution is necessary, it is equally well applicable as Eq. (55) what can also be seen from Table III. Thus, we can confirm that the computation time for observables of the type $A_L(\vec{r})$ can be kept small compared with the time needed for the MO-calculation. For only one-center and at most resonance integrals have to be evaluated exactly, while crystal-field integrals and three-center integrals can be treated on the level of point-charge approximations.

We will conclude the discussion of inverse moment integrals with some comments concerning the resonance integrals. Again from Table III it can be seen that the bond-pca works quite well in many cases and from previous investigations on ESCA chemical shifts¹⁷⁻¹⁹. The diamagnetic shielding of nuclei²⁰ also confirm this conclusion even in case of the valence-pca. However, it should be recognised that these integrals depend strongly on the actual shape of $a_l(\vec{r})$. Additionally, our calculations have shown that independently of $a_l(\vec{r})$ for higher inverse moments the bond-pca becomes worse with increasing l in accordance with our former results on electric field gradient calculations¹⁰.

V. TOTAL ENERGIES

The total energy is a quantity of central interest in molecular electronic structure theory, since firstly the equilibrium geometry and the binding energy of a molecule can be derived from it. Secondly, the calculation of geometries is one of the essential applications of any molecular orbital theory being a crucial proof for its usefulness. Moreover, we have a sensitive test for the validity of the various point-charge approximations because the energy variation around the equilibrium geometry produces small relative changes of large numbers.

In $X\alpha$ approximation the total energy is given as³

$$\begin{aligned} \langle EX\alpha \rangle = & \sum_k n_k \int \psi_k^*(\vec{r}) h_0 \psi_k(\vec{r}) d^3r + \iint \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r d^3r' + \\ & + \frac{3}{4} \int \rho(\vec{r}) V_{\text{ex}}(\vec{r}) d^3r + \frac{1}{2} \sum'_{xy} \frac{2Z_x Z_y}{R_{xy}} = H_0 + \frac{1}{2} E_{\text{cb}} + \frac{3}{4} E_{\text{ex}} + E_{\text{ion}} \quad (58) \end{aligned}$$

On the other hand, from the Schrödinger equation

$$[h_0 + 2 \int \frac{\rho(\vec{r}') d^3r'}{|\vec{r} - \vec{r}'|} + V_{\text{ex}}(\vec{r})] \psi_k(\vec{r}) = \epsilon_k \psi_k(\vec{r}) \quad (59)$$

follows

$$H_0 + E_{cb} + E_{ex} = \sum_k n_k \varepsilon_k \quad (60)$$

yielding together with Eq. (58)

$$\langle EX\alpha \rangle = \sum_k n_k \varepsilon_k - \frac{1}{2} (E_{cb} + \frac{1}{2} E_{ex}) + E_{ion} \quad (61)$$

We want to discuss in more detail the Coulomb term which can be written as

$$\frac{1}{2} E_{cb} = \langle V_{cb} \rangle = \sum_k n_k \langle \psi_k | \int \frac{\rho(\vec{r}') d^3r'}{|\vec{r} - \vec{r}'|} | \psi_k \rangle \quad (62)$$

Assuming an in the SCC— $X\alpha$ approximation strict core-valence separability together with the core-pca, *i. e.*

$$\rho^{co}(\vec{r}) + \rho^{val}(\vec{r}) = \rho(\vec{r}) \quad \text{and} \quad \rho^{co}(\vec{r}) = \sum_x N_x^{co} \delta(\vec{r} - \vec{R}_x)$$

the electronic Coulomb interaction is transformed to

$$\langle V_{cb} \rangle = \sum_{val} n_k \langle \psi_k | \int \frac{\rho^{val}(\vec{r}') d^3r'}{|\vec{r} - \vec{r}'|} + 2 \sum_x \frac{N_x^{co}}{|\vec{r} - \vec{R}_x|} | \psi_k \rangle + \sum'_{xv} \frac{N_x^{co} N_v^{co}}{R_{xv}} \quad (63)$$

Representing the valence density again with a single exponential as in section II, and applying the LCAO approximation on the first term we obtain

$$\langle V_{cb} \rangle = \sum_{\mu\nu} \sum_{ij} P_{ij}^{\mu\nu} \sum_x \langle \phi_i(\mu) | W_x(|\vec{r} - \vec{R}_x|) + \frac{2 N_x^{co}}{|\vec{r} - \vec{R}_x|} | \phi_j(\nu) \rangle + \sum'_{xv} \frac{N_x^{co} N_v^{co}}{R_{xv}} \quad (64)$$

where

$$W_x(r) = \frac{N_x^{val}}{r} (1 - e^{-\eta_x r}) - \frac{1}{2} N_x^{val} \eta_x e^{-\eta_x r} \quad (65)$$

It should be mentioned that N_x^{val} does generally not equal the number of valence electrons in the free atom, but is an effective electron number, *i. e.* $N_x^{val} = N_{at}^{val} - Q_x$, where Q_x is the effective charge. The final result for the total energy in the SCC— $X\alpha$ approximation may thus be written as

$$\langle EX\alpha \rangle_{SCC} = \sum_{val} n_k \varepsilon_k^{val} + \sum_{core} n_k \varepsilon_k^{co} + \sum'_{xv} \frac{Z_x Z_v - N_x^{co} N_v^{co}}{R_{xv}} - \langle V_{ee} \rangle$$

$$\langle V_{ee} \rangle = \sum_{\mu\nu} \sum_{ij} P_{ij}^{\mu\nu} \langle \phi_i(\mu) | \sum_x [W_x(|\vec{r} - \vec{R}_x|) + \frac{2 N_x^{co}}{|\vec{r} - \vec{R}_x|}] + \frac{1}{4} V_{ex} | \phi_j(\nu) \rangle \quad (66)$$

From this equation the various types of point-charge approximations are easily derived by applying this to $W_x(r)$ and assuming that the exchange part ap-

proximately cancels the self interaction energy term. Then $\langle V_{ee} \rangle$ takes the form

$$\langle V_{ee} \rangle = \sum_{\mu\nu} \sum_{ij} P_{ij}^{\mu\nu} \langle \phi_i^{(\mu)} | \sum'_x \frac{N_x^{\text{val}} + 2 N_x^{\text{co}}}{|\vec{r} - \vec{R}_x|} | \phi_j^{(\nu)} \rangle \quad (67)$$

where the prime on the summation means that $x \neq \nu$ for $\mu = \nu$. In the valence-pca we obtain now

$$\langle V_{ee} \rangle_{\text{v-pca}} = \sum_{\mu\nu} \sum_{ij} P_{ij}^{\mu\nu} \sum_{\substack{x \\ (\neq \nu)}} \frac{N_x^{\text{val}} + 2 N_x^{\text{co}}}{R_{x\nu}} S_{ij}^{\mu\nu} = \sum'_{x\nu} \frac{N_\nu^{\text{val}} (N_x^{\text{val}} + 2 N_x^{\text{co}})}{R_{x\nu}} \quad (68)$$

which is seen to cancel exactly with the third term on the right hand side of Eq. (66) only in nonpolar molecules, *i. e.* when N^{val} equals the number of valence electrons in the respective free atom. This shows clearly that even in valence-pca the total energy cannot be generally assumed to be simply equal to the sum of the one-electron eigenvalues. Instead the following expression has to be used

$$\langle EX\alpha \rangle_{\text{v-pca}} = \sum_{\text{val}} n_k \varepsilon_k + \sum'_{x\nu} \frac{Z_x Z_\nu - (N_x^{\text{co}} + N_x^{\text{val}}) (N_\nu^{\text{co}} + N_\nu^{\text{val}})}{R_{x\nu}} \quad (69)$$

The corresponding equation in the bond-pca, in which the overlap charges are retained, reads finally as

$$\begin{aligned} \langle EX\alpha \rangle_{\text{b-pca}} = & \sum_{\text{val}} n_k \varepsilon_k + \sum'_{x\nu} \frac{Z_x Z_\nu - N_x^{\text{co}} N_\nu^{\text{co}} - N^{\nu\nu} (N_x^{\text{val}} + 2 N_x^{\text{co}})}{R_{x\nu}} \\ & - \sum'_{\mu\nu} N_{\mu\nu} \left[\frac{N_\mu^{\text{val}} + 2 N_\mu^{\text{co}}}{R_{\mu\nu}} + \frac{N_\nu^{\text{val}} + 2 N_\nu^{\text{co}}}{R_{\mu\nu}} + \sum'_{\substack{x \\ (\neq \mu, \nu)}} \frac{N_x^{\text{val}} + 2 N_x^{\text{co}}}{R_{x\nu}} \right] \quad (70) \end{aligned}$$

The equations (66), (69) and (70) have been tested now in computing the equilibrium geometries of the seven molecules C_2 , N_2 , F_2 , Cl_2 , Br_2 , CO , and H_2O . The first remarkable common property of both the valence-pca as well as the bond-pca is the fact that no minimum has been obtained for all molecules; the same is true for the eigenvalue sum. For this reason, only Eq. (66) will be discussed in more detail by means of Table IV where the various contributions to the total valence energy are listed separately according to Eq. (66) together with our discussion of the A_{00} matrix elements in section IV. The crystal-field integrals have been split into the spherical and the aspherical terms, respectively, arising from the partial wave expansion to demonstrate the nonnegligibility of the latter ones in this case. For, although their absolute values do not exceed 10% of the spherical counterparts, the bond length in N_2 *e. g.* will be shortened by approximately 0.1 a. u. as can be seen from the last two columns of Table IV. Additionally, when omitting the core energies the sum of all terms, apart from the resonance parts, cancel almost exactly around the equilibrium position, while the latter ones show themselves a minimum, making thus a careful evaluation of these integrals necessary. From this it may also be comprehensible why the point charge approximations do not work, since the accurate resonance integrals are especially important.

TABLE IV
 Contributions to the Total SCC-X α Valence Energy as a Function of Distance for N₂. Energies are Given in R_y, Distances
 in Bohr Units

R	Eigenvalue sum	Ionic	Core-core	Spher. c-f-contr.			Aspher. c-f-contr.			Sum of 1-7	Resonance contr.			Total energy	Total energy - aspher. c-f-contr.
				core-val	val-val	core-val	val-val	core-val	val-val		core-val	val-val			
1.77	-16.33	55.34	-4.52	-18.19	-17.87	0.70	0.75	-0.11	-9.70	-11.30	-21.11	-19.66			
1.87	-15.74	52.38	-4.28	-17.06	-17.05	1.11	1.06	0.42	-10.51	-12.18	-22.27	-20.10			
1.97	-15.24	49.72	-4.06	-16.21	-16.52	1.32	1.25	0.27	-10.63	-12.33	-22.69	-20.12			
2.07	-14.81	47.32	-3.86	-15.54	-16.15	1.41	1.35	-0.27	-10.36	-12.05	-22.68	-19.92			
2.17	-14.45	45.14	-3.68	-14.96	-15.85	1.42	1.39	-0.99	-9.88	-11.54	-22.41	-19.60			
2.27	-14.14	43.15	-3.52	-14.47	-15.59	1.38	1.39	-1.80	-9.29	-10.90	-21.99	-19.22			
2.37	-13.87	41.33	-3.37	-14.03	-15.36	1.31	1.36	-2.62	-8.65	-10.20	-21.47	-18.80			

TABLE V

Comparison of Experimental and Calculated Equilibrium Geometries. All Distances in Bohr Units

Molecule	Experimental	Calculated	%-Deviation
C ₂	2.35	2.27	3
N ₂	2.07	2.02	2
F ₂	2.68	2.92	9
Cl ₂	3.76	3.99	6
Br ₂	4.31	4.18	3
CO	2.13	2.06	3
H ₂ O	1.81	1.74	4
	104.5	108.0	3

In going next to the calculated equilibrium geometries (cf. Table V), the SCC— $X\alpha$ method turns out to be able to produce values with a deviation of less than 10% from the respective experimental ones. This error interval is in accordance with our previous experience from other calculated observable quantities as ionisation potentials, dipole moments, ESCA- and Mössbauer isomer-shifts, and electric field gradients. At first sight it might be surprising that on the basis of such a crude approximation geometries can be computed with such a degree of accuracy. Particularly because the results are non-fitted in the sense of having determined the necessary parameters from other previous calculations. The main reason for this success can be found I think in the fact that the angular parts of all the matrix elements have been evaluated analytically, *i. e.* the molecular symmetry is reproduced exactly, while the parameters only enter the radial integrals which cannot anyway be determined accurately even in *ab initio* methods due to *e. g.* the Hartree-Fock and the LCAO-approximations. This belief results from the experience with such a simple model as the crystal field theory of Bethe and van Vleck²¹ which is able to reproduce the central ion bands of the optical spectra of complex ions due to symmetry arguments only, provided the radial integrals are handled as free adjustable parameters. Additionally, it has been shown recently that total SCF energies can be represented surprisingly well in the *pca*²² although the results are still far from chemical accuracy.

Beyond that one has to conclude that the SCC— $X\alpha$ parametrisation scheme apparently fulfills to a high degree the basic necessary condition for any semiempirical theory, namely an almost perfect cancellation of unknown errors.

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SAŽETAK

Primjenljivost aproksimacije točkastog naboja pri računanju očekivanih vrijednosti za molekule

Michael Grodzicki

Ispitana je mogućnost računanja prosječnih vrijednosti različitih molekulskih svojstava s pomoću aproksimacije točkastih naboja (PCA). Pri tome je raspodjela elektronske gustoće generirana primjenom izvorne $X\alpha$ -metode samouskladenog naboja. Pokazano je da se samo neka svojstva mogu uspješno izračunati u PCA-aproksimaciji. PCA ne zadovoljava za računanje ukupne energije i molekulske geometrije, pa se odgovarajući matricni elementi moraju mnogo točnije odrediti.