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Effective hamiltonian for the molecular binding

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Abstract

Extended bond-like orbitals are included in molecular-like orbitals, beside the localized atomic-like orbitals, and an effective hamiltonian governing the chemical bond is derived; the derivation is based upon the difference between the atomic- and bond-scale lengths. The effective hamiltonian introduces the interaction between the electrons participating in chemical bond and their electronic "holes" in the atomic-like orbitals. A fractional occupancy is established for the bond-like orbitals, which is specific to the chemical bond.

Atomic aggregates like molecules, atomic clusters or solids consist of atomic nuclei and electrons interacting through Coulomb forces (relativistic corrections may be left aside to a first approximation); a particular case is represented by the many-electron atoms. Wavefunctions methods have been developed both for the atomic and the chemical bond, based on the Hartree-Fock equations for single-electron states.[1] The chemical bond is usually described by superpositions of atomic-like single-electron orbitals (or equivalent sets of basis wavefunctions),[2] though molecular-like orbitals have been pointed out from the early days of the chemical bond theories.[3] Density-functionals methods[4] touch upon this point, especially in connection with the Thomas-Fermi model.[5] An effective hamiltonian for the chemical bond is derived here, which provides a description of the atomic aggregates within the quasi-classical theory and the linearized Thomas-Fermi model of a slightly inhomogeneous electron liquid.[6]$^-$[7]

An ensemble of N atoms with atomic numbers Z_i and the nuclei placed at positions $\mathbf{R}_i$, $i = 1, 2, ...N$, is described by the hamiltonian

$$
\begin{aligned}
H \;=\; & \sum_\alpha \mathbf{p}_\alpha^2/2m - \sum_{i\alpha} \frac{e^2 Z_i}{|\mathbf{R}_i - \mathbf{r}_\alpha|} + \frac{1}{2} \sum_{\alpha \neq \beta} \frac{e^2}{|\mathbf{r}_\alpha - \mathbf{r}_\beta|} + \\
& + \frac{1}{2} \sum_{i \neq j} \frac{e^2 Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|} \quad ,
\end{aligned}
\tag{1}
$$

where $\mathbf{r}_\alpha$ and $\mathbf{p}_\alpha$ denote the position and, respectively, the momentum of the α-th electron, m is the electron mass and $-e$ is the electron charge; equation (1) includes the kinetic energy of the electrons, the electron-nuclei Coulomb attraction, the electron-electron and the inter-nuclei Coulomb repulsions; for the sake of the simplicity the atomic units Bohr radius $a_H = \hbar^2/2m = 0.53$Å for lengths and $e^2/a_H = 27.2$eV for energy will be used.

Making use of molecular-like orbitals $\psi_s(\mathbf{r})$ for single-electron states denoted by s, the Hartree-Fock energy functional reads

$$
\begin{aligned}
E \;=\; & \int d\mathbf{r} \sum_s \psi_s^*(\mathbf{p}^2/2)\psi_s - \int d\mathbf{r} \sum_i (Z_i/|\mathbf{R}_i - \mathbf{r}|) \sum_s \psi_s^*\psi_s + \\
& + \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'(1/|\mathbf{r}-\mathbf{r}'|) \sum_s \psi_s^*\psi_s \cdot \sum_{s'} \psi_{s'}^*\psi_{s'} - \\
& - \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'(1/|\mathbf{r}-\mathbf{r}'|) \sum_s \psi_s^*(\mathbf{r})\psi_s(\mathbf{r}') \cdot \sum_{s'} \psi_{s'}^*(\mathbf{r}')\psi_{s'}(\mathbf{r}) + \\
& + \frac{1}{2}\sum_{i\neq j} Z_i Z_j/|\mathbf{R}_i - \mathbf{R}_j| \quad,
\end{aligned}
\tag{2}
$$

where one may identify the direct (Hartree) interaction, expressed with the electron density $\sum_s \psi_s^*\psi_s$, and the exchange (Fock, Dirac) contribution, written in terms of the bi-local "electron density" $\sum_s \psi_s^*(\mathbf{r})\psi_s(\mathbf{r}')$.

The molecular-like orbitals ψ_s (spin included) consist of a superposition

$$
\psi_s = \varphi_s + \Phi_s
\tag{3}
$$

of localized atomic-like orbitals φ_s and extended orbitals Φ_s; the latter may be called bond-like orbitals; such a superposition may ensure the completeness of the single-electron wavefunctions; the two sets of orbitals may be taken as being orthogonal to each other (like the orbitals within each set, too). The atomic-like orbitals φ_s (or their linear combinations) are localized over atomic-scale lengths, while the bond-like orbitals Φ_s extends over the size of the atomic aggregates. Because of this great disparity in the scale lengths of the two sets of orbitals most of the matrix elements in the energy functional (2) are small and, consequently, they may be neglected; this holds for the off-diagonal matrix elements of the kinetic energy and for the interaction terms where cross-contributions like $\varphi_s \Phi_s$ both to the electron density and to its bi-local generalization may be neglected; in addition, cross-contributions to the exchange energy of the form $\varphi_s^*(\mathbf{r})\varphi_s(\mathbf{r}') \cdot \Phi_{s'}^*(\mathbf{r}')\Phi_{s'}(\mathbf{r})$ are also small contributions which may be neglected (in this respect the bi-local "electron density" exhibits a wavefunction character rather than a true particle-density character). Under these circumstances the energy functional E splits into an atomic-like energy functional E_a, a bond-like energy functional E_b, and an interaction contribution E_{ab} originating in the density-density quadratic direct interaction in (3); indeed, in general, the variation of the particle density is smaller than the variation of the wavefunctions; therefore, one may write

$$
E = E_a + E_b + E_{ab} \quad,
\tag{4}
$$

where

$$
\begin{aligned}
E_a \;=\; & \int d\mathbf{r} \sum_s \varphi_s^*(\mathbf{p}^2/2)\varphi_s - \int d\mathbf{r} \sum_i (Z_i/|\mathbf{R}_i - \mathbf{r}|) \sum_s \varphi_s^*\varphi_s + \\
& + \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'(1/|\mathbf{r}-\mathbf{r}'|) \sum_s \varphi_s^*\varphi_s \cdot \sum_{s'} \varphi_{s'}^*\varphi_{s'} - \\
& - \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'(1/|\mathbf{r}-\mathbf{r}'|) \sum_s \varphi_s^*(\mathbf{r})\varphi_s(\mathbf{r}') \cdot \sum_{s'} \varphi_{s'}^*(\mathbf{r}')\varphi_{s'}(\mathbf{r}) + \\
& + \frac{1}{2}\sum_{i\neq j} Z_i Z_j/|\mathbf{R}_i - \mathbf{R}_j|
\end{aligned}
\tag{5}
$$

is the atomic-like energy functional (including the inter-nuclei Coulomb repulsion),

$$
E_b = \int d\mathbf{r} \sum_s \Phi_s^* (\mathbf{p}^2/2) \Phi_s - \int d\mathbf{r} \sum_i (Z_i/|\mathbf{R}_i - \mathbf{r}|) \sum_s \Phi_s^* \Phi_s +
$$

$$
+ \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' (1/|\mathbf{r} - \mathbf{r}'|) \sum_s \Phi_s^* \Phi_s \cdot \sum_{s'} \Phi_{s'}^* \Phi_{s'} - \tag{6}
$$

$$
- \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' (1/|\mathbf{r} - \mathbf{r}'|) \sum_s \Phi_s^* (\mathbf{r}) \Phi_s(\mathbf{r}') \cdot \sum_{s'} \Phi_{s'}^* (\mathbf{r}') \Phi_{s'}(\mathbf{r})
$$

is the bond-like energy functional, and

$$
E_{ab} = \int d\mathbf{r} d\mathbf{r}' (1/|\mathbf{r} - \mathbf{r}'|) \sum_s \varphi_s^* \varphi_s \cdot \sum_{s'} \Phi_{s'}^* \Phi_{s'} \tag{7}
$$

is the interaction between the atomic- and bond-like orbitals.

It is more convenient now to highlight the usual linear-combination coefficients α_s and β_s trough the substitutions $\varphi_s \to \alpha_s \varphi_s$ and $\Phi_s \to \beta_s \Phi_s$, which obey the normalization condition

$$
\alpha_s^2 + \beta_s^2 = 1 \tag{8}
$$

(the complex nature of these coefficients is irrelevant), and use wavefunctions φ_s and Φ_s which are normalized, $\int d\mathbf{r} \cdot |\varphi_s|^2 = 1$, $\int d\mathbf{r} \cdot |\Phi_s|^2 = 1$; the energy functionals above can then be written as

$$
E_a = \sum_s \alpha_s^2 t_s^a - \sum_s \alpha_s^2 n_s^a + \frac{1}{2} \sum_{ss'} \alpha_s^2 \alpha_{s'}^2 d_{ss'}^a -
$$

$$
\tag{9}
$$

$$
- \frac{1}{2} \sum_{ss'} \alpha_s^2 \alpha_{s'}^2 e_{ss'}^a + \frac{1}{2} \sum_{i \neq j} Z_i Z_j / |\mathbf{R}_i - \mathbf{R}_j|
$$

for the atomic-like part,

$$
E_b = \sum_s \beta_s^2 t_s^b - \sum_s \beta_s^2 n_s^b + \frac{1}{2} \sum_{ss'} \beta_s^2 \beta_{s'}^2 d_{ss'}^b -
$$

$$
\tag{10}
$$

$$
- \frac{1}{2} \sum_{ss'} \beta_s^2 \beta_{s'}^2 e_{ss'}^b
$$

for the bond-like part, and

$$
E_{ab} = \frac{1}{2} \sum_{ss'} \alpha_s^2 \beta_{s'}^2 d_{ss'}^{ab} \tag{11}
$$

for the mixed term (7) in the energy functional, where the following notations have been introduced: the kinetic energies

$$
t_s^a = \int d\mathbf{r} \varphi_s^* (\mathbf{p}^2/2) \varphi_s \;\; , \;\; t_s^b = \int d\mathbf{r} \Phi_s^* (\mathbf{p}^2/2) \Phi_s \tag{12}
$$

of the single-electron states in both types of orbitals (atomic-like and, respectively, bond-like orbitals); the electron-nuclei energies

$$
n_s^a = \int d\mathbf{r} \sum_i (Z_i/|\mathbf{R}_i - \mathbf{r}|) \varphi_s^* \varphi_s \;\; , \;\; n_s^b = \int d\mathbf{r} \sum_i (Z_i/|\mathbf{R}_i - \mathbf{r}|) \Phi_s^* \Phi_s \tag{13}
$$

of similar single-electron states; the (symmetric) direct

$$d_{ss'}^a = \int d\mathbf{r} d\mathbf{r}' (1/|\mathbf{r} - \mathbf{r}'|) \varphi_s^* \varphi_s \cdot \varphi_{s'}^* \varphi_{s'} \quad ,$$

$$d_{ss'}^b = \int d\mathbf{r} d\mathbf{r}' (1/|\mathbf{r} - \mathbf{r}'|) \Phi_s^* \Phi_s \cdot \Phi_{s'}^* \Phi_{s'}$$

(14)

and exchange

$$e_{ss'}^a = \int d\mathbf{r} d\mathbf{r}' (1/|\mathbf{r} - \mathbf{r}'|) \varphi_s^*(\mathbf{r}) \varphi_s(\mathbf{r}') \cdot \varphi_{s'}^*(\mathbf{r}') \varphi_{s'}(\mathbf{r}) \quad ,$$

$$e_{ss'}^b = \int d\mathbf{r} d\mathbf{r}' (1/|\mathbf{r} - \mathbf{r}'|) \Phi_s^*(\mathbf{r}) \Phi_s(\mathbf{r}') \cdot \Phi_{s'}^*(\mathbf{r}') \Phi_{s'}(\mathbf{r})$$

(15)

interaction matrices; and finally the symmetric matrix

$$d_{ss'}^{ab} = \int d\mathbf{r} d\mathbf{r}' (1/|\mathbf{r} - \mathbf{r}'|) (\varphi_s^* \varphi_s \cdot \Phi_{s'}^* \Phi_{s'} + \varphi_{s'}^* \varphi_{s'} \cdot \Phi_s^* \Phi_s) \tag{16}$$

of the direct interaction between the atomic-like orbitals and the bond-like orbitals.

One may substitute now $\alpha_s^2 = 1 - \beta_s^2$ as given by (8) into E_a and E_{ab} above, and obtains

$$
\begin{aligned}
E_a &= \sum_s (t_s^a - n_s^a) + \frac{1}{2} \sum_{ss'} (d_{ss'}^a - e_{ss'}^a) + \\
&\quad + \frac{1}{2} \sum_{i \neq j} Z_i Z_j / |\mathbf{R}_i - \mathbf{R}_j| - \\
&\quad - \sum_s \beta_s^2 (t_s^a - n_s^a + \sum_{s'} d_{ss'}^a - \sum_{s'} e_{ss'}^a) + \\
&\quad + \frac{1}{2} \sum_{ss'} \beta_s^2 \beta_{s'}^2 (d_{ss'}^a - e_{ss'}^a)
\end{aligned}
$$

(17)

and

$$E_{ab} = \frac{1}{2} \sum_{ss'} \beta_{s'}^2 d_{ss'}^{ab} - \frac{1}{2} \sum_{ss'} \beta_s^2 \beta_{s'}^2 d_{ss'}^{ab} \quad ; \tag{18}$$

it is worth noting here the occurrence of an attraction between the bond-like electrons and the atomic-like electronic "holes", as expressed by the quartic $\beta_s^2 \beta_{s'}^2$-term in E_{ab}. The β_s-dependent part of the total energy $E = E_a + E_b + E_{ab}$ is now a general quadratic form (*i.e.* a quadratic form plus a linear form) in β_s^2; its minimum values are obtained for those β_s^2-parameters that satisfy a system of linear equations of the form

$$-A_s + \sum_{s'} D_{ss'} \beta_{s'}^2 = 0 \quad , \tag{19}$$

where

$$
\begin{aligned}
A_s &= (t_s^a - n_s^a + \sum_{s'} d_{ss'}^a - \sum_{s'} e_{ss'}^a) - (t_s^b - n_s^b) - \frac{1}{2} \sum_{s'} d_{ss'}^{ab} = \\
&= \varepsilon_s^a(HF) - \varepsilon_s^b(HF) + \sum_{s'} (d_{ss'}^b - e_{ss'}^b - \frac{1}{2} d_{ss'}^{ab}) \quad ,
\end{aligned}
$$

(20)

the D-matrix is given by

$$D_{ss'} = (d^a_{ss'} - e^a_{ss'}) + (d^b_{ss'} - e^b_{ss'}) - d^{ab}_{ss'} \quad , \tag{21}$$

and

$$\varepsilon^{a,b}_s(HF) = t^{a,b}_s - n^{a,b}_s + \sum_{s'} d^{a,b}_{ss'} - \sum_{s'} e^{a,b}_{ss'} \tag{22}$$

are the Hartree-Fock single-electron energies of the atomic-like and, respectively, bond-like orbitals.

The solutions of equations (19) may give, in principle, the molecular-like bond of an atomic aggregate, *i.e.* the stability and the equilibrium of such an aggregate as described by the molecular-like binding; the existence of solutions for equations (19) may be viewed as the core of the general solution to the chemical bond; at the same time, equations (19) may also be viewed as providing the criterion of chemical binding through molecular-like orbitals. The detailed analysis of equations (19) is a matter of specific investigation; however, their general structure lends itself to a qualitative discussion given below.

First, one may note that in view of the disparity between the atomic- and bond-scale lengths the mixed-direct interaction $d^{ab}_{ss'}$ between the two types of orbitals is small in comparison with the other contributions to $D_{ss'}$ in (21); secondly, the exchange energies are usually smaller than the direct energies, as a consequence of their delocalization character; therefore, one may assume that, very likely, $D_{ss'}$ is a positive definite matrix. It follows that A_s in (19) must have positive values in order to have a solution for β^2_s ($0 < \beta^2_s < 1$). However, for inner atomic states the Hartree-Fock energies have large negative values (due mainly to the large electron-nucleus attraction n^a_s), so that the corresponding A_s quantities acquire negative values in this case, and equations (19) have no solutions ($\beta^2_s = 0$); the inner atomic shells do not provide (spontaneously) electrons for participating in the chemical bond, as expected. The discussion will therefore be restricted for the moment to the upper atomic shells. For the ideal case of atoms separated at infinite, *i.e.* for independent atoms, the highest Hartree-Fock energy of the atomic-like orbitals, *i.e.* the chemical potential of the electrons in atoms, has negative values, while all the quantities in (20) related to the bond-like orbitals vanish; it follows that equations (19) have no solution in this case either, as expected; indeed, rigorously isolated atoms are stable, they could not tend to bind together. Getting the atoms closer to one another the atomic-like orbitals φ_s become superpositions of single-atom orbitals χ_a localized ar $\mathbf{R}_i$,

$$\varphi_s(\mathbf{r}) = \sum_{ia} c^s_{ia} \chi_a(\mathbf{r} - \mathbf{R}_i) \quad , \tag{23}$$

so that the matrix elements given in (12)-(16) acquire a dependence on the inter-nuclei distances;[8] in addition, the Hartree-Fock energy levels of the upper electronic shells in the individual atoms split now in energy bands, while the chemical potential $\varepsilon^b_s(HF)$ of the bond-like electrons in (20) acquires lower values; under such circumstances some of the A_s quantities, corresponding to the upper levels, may acquire positive values, and the corresponding atomic-like orbitals tend to participate with electrons in the chemical bond; in this case equations (19) may have a few non-vanishing solutions for small values of the parameters β^2_s, and the chemical bond may appear thereby, as described by the bond-like part of the energy functional $E = E_a + E_b + E_{ab}$ given by (10), (17) and (18).

It is convenient to write the total energy functional as $E = E_1 + E_2$, where E_1 includes the entire E_b without the electron-nuclei attraction (which is included in E_2), plus all the quartic

$\beta_s^2\beta_{s'}^2$-terms in E_a and E_{ab}; the remaining terms are included in E_2; in other words, all the quartic $\beta_s^2\beta_{s'}^2$-contributions to the total energy functional are included in E_1 plus the kinetic energy of the bond-like electrons; while all the remaining contributions are relegated to E_2. One obtains

$$E_1 = \sum_s \beta_s^2 t_s^b - \frac{1}{2}\sum_{ss'}\beta_s^2\beta_{s'}^2 d_{ss'}^{ab} + \frac{1}{2}\sum_{ss'}\beta_s^2\beta_{s'}^2 d_{ss'}^b -$$
$$-\frac{1}{2}\sum_{ss'}\beta_s^2\beta_{s'}^2 e_{ss'}^b + \frac{1}{2}\sum_{ss'}\beta_s^2\beta_{s'}^2(d_{ss'}^a - e_{ss'}^a) \tag{24}$$

and

$$E_2 = \sum_s(t_s^a - n_s^a) + \frac{1}{2}\sum_{ss'}(d_{ss'}^a - e_{ss'}^a) +$$
$$+\frac{1}{2}\sum_{i\neq j} Z_i Z_j / |\mathbf{R}_i - \mathbf{R}_j| -$$
$$-\sum_s \beta_s^2(t_s^a - n_s^a + \sum_{s'} d_{ss'}^a - \sum_{s'} e_{ss'}^a) -$$
$$-\sum_s \beta_s^2(n_s^b - \frac{1}{2}\sum_{s'} d_{ss'}^{ab}) \; ; \tag{25}$$

making use of (19)-(22) the energy E_2 can also be written as

$$E_2 = \sum_s(t_s^a - n_s^a) + \frac{1}{2}\sum_{ss'}(d_{ss'}^a - e_{ss'}^a) +$$
$$+\frac{1}{2}\sum_{i\neq j} Z_i Z_j / |\mathbf{R}_i - \mathbf{R}_j| - \sum_s \beta_s^2(A_s + t_s^b) \; ; \tag{26}$$

it is worth noting that E_2 contains a purely atomic-like energy, plus the last contribution to (26) which may also be written as $-\sum_s \beta_s^2 t_s^b - \sum_{ss'} D_{ss'}\beta_s^2\beta_{s'}^2$; it is also worth emphasizing that the attraction between the bond-like electrons and the bare nuclei (the n_s^b-term) does not appear in the equilibrium expressions of the energy functionals $E_{1,2}$, as a consequence of the minimization of the β_s^2-quadratic form, expressed by equations (19). In addition, one may also note that the presence of the kinetic energy of the bond-like electrons (t_s^b-terms) both in the last term in E_2 and in the bond-like energy functional E_1 is related to the molecular-like extension (3) of the electron dynamics, such as to include the contribution of the extended bond-like orbitals Φ_s.

It is easy now to identify the effective hamiltonian corresponding to the bond-like energy functional given by (24); first, one may note in (24) the fractional occupancy factor β_s^2 of the bond-like orbitals Φ_s, which, according to the discussion above, is non-vanishing ($\beta_s^2 \neq 0$) only for a limited number of upper energy levels, corresponding to atomic-like orbitals a in the upper atomic shells; it is convenient to introduce the density

$$\rho = \sum_s \beta_s^2 \varphi_s^* \varphi_s \tag{27}$$

of electronic "holes" in the ionic cores, *i.e.* the density of positive charge in the upper atomic shells, and note that the energy functional E_1 includes the kinetic energy of the bond-like electrons

(first term in (24)), the attraction between the bond-like electrons and the positively-charged ionic cores (the second term in (24)), the Coulomb repulsion between the bond-like electrons (the third term and the fourth term (24)), and finally, the Coulomb repulsion between the ionic cores (last term in (24); a bi-local atomic-like density similar with (27) may formally be used here for the exchange inter-ionic energy); therefore, according to (24), the effective hamiltonian of the bond-like electrons reads

$$
H_b = \sum_\alpha \mathbf{p}_\alpha^2/2m - \sum_\alpha \int d\mathbf{r}' \cdot \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}_\alpha|} + \frac{1}{2} \sum_{\alpha \neq \beta} \frac{1}{|\mathbf{r}_\alpha - \mathbf{r}_\beta|} +
$$

$$
+\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \cdot \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} \quad . \tag{28}
$$

Making use of (23) the ionic charge density may be written as

$$
\rho = \sum_{ias} \beta_s^2 \left| c_{ia}^s \chi_{ia} \right|^2 \quad , \tag{29}
$$

where χ_{ia} is the atomic orbital $\chi_a(\mathbf{r} - \mathbf{R}_i)$ centered on $\mathbf{R}_i$, and the contribution of the mixed terms has been neglected; introducing the notation $\alpha_{ia} = \sum_s \beta_s^2 \left| c_{ia}^s \right|^2$ one may also write

$$
\rho = \sum_{ia} \alpha_{ia} \left| \chi_{ia} \right|^2 \quad , \tag{30}
$$

which gives an effective charge

$$
z_i^* = \sum_a \alpha_{ia} \tag{31}
$$

for every atom; for a point-like charge distribution of the ionic cores $\rho(\mathbf{r}) = \sum_i z_i^* \delta(\mathbf{r} - \mathbf{R}_i)$, the effective hamiltonian (28) becomes

$$
H_b = \sum_\alpha \mathbf{p}_\alpha^2/2m - \sum_{i\alpha} \cdot \frac{z_i^*}{|\mathbf{R}_i - \mathbf{r}_\alpha|} + \frac{1}{2} \sum_{\alpha \neq \beta} \frac{1}{|\mathbf{r}_\alpha - \mathbf{r}_\beta|} +
$$

$$
+\frac{1}{2} \sum_{i \neq j} \frac{z_i^* z_j^*}{|\mathbf{r}' - \mathbf{r}|} \quad , \tag{32}
$$

which has been employed in Refs.6 and 7 for the metallic bond.

The mixed terms may be preserved, in general, in the ionic charge density (27), in contrast to the simplified expression (29); in that case, the ionic cores density of positive charge reads

$$
\rho = \sum_{ia;jb} \alpha_{ia;jb} \chi_{ia}^* \chi_{jb} \quad , \tag{33}
$$

where

$$
\alpha_{ia;jb} = \sum_s \beta_s^2 c_{ia}^{s*} c_{jb}^s \quad ; \tag{34}
$$

hence, the charge of electronic "holes" on each atomic orbital is

$$
z_{ia}^* = \alpha_{ia;ia} = \sum_s \beta_s^2 \left| c_{ia}^s \right|^2 \quad , \tag{35}
$$

according to the orthogonality of the atomic-like orbitals χ_{ia}; these charges are not point-like charges in general, but their pair-like distribution is given by (33). The bond-like hamiltonian

(28) leads to a quasi-classical description of a slightly inhomogeneous electron liquid, where atomic-like contribution is usually neglected and the bond-like orbitals Φ_s are (quasi-) plane waves in the first approximation; under these circumstances the minimum value of the energy is realized by an unrestricted occupancy of these orbitals (*i.e.* $\beta_s^2 = 1$ in the quasi-classical conterpart of the energy functonal E_1), while the conservation of the total charge is ensured by the Coulomb interactions in (28); indeed, the total charge of the ionic cores described by the density ρ given by (27) is equal to the total charge of the bond-like electrons, as expected. Such a treatment is appropriate for the cohesion, the equilibrium structure and the binding energy of the atomic aggregate, as described within the quasi-classical theory and the linearized Thomas-Fermi model; however, the occupancy factor must be explicitly employed for the single-electron properties, as, for instance, in computing the ionization potential, or the plasmon frequency of such atomic aggregates; one may say that the bond-like electrons are "strongly renormalized" (fractional occupancy β_s^2) by their interaction with the ionic cores.[6],[7]

The atomic fractional occupancy α_s^2 can be made explicit by recasting the energy functional E_2 given by (25) or (26) as

$$
\begin{aligned}
E_2 &= \sum_s \alpha_s^2 (t_s^a - n_s^a) + \frac{1}{2} \sum_{ss'} \alpha_s^2 \alpha_{s'}^2 (d_{ss'}^a - e_{ss'}^a) + \\
&\quad + \frac{1}{2} \sum_{i \neq j} Z_i Z_j / |\mathbf{R}_i - \mathbf{R}_j| - \\
&\quad - \sum_{ss'} \beta_s^2 \beta_{s'}^2 D_{ss'} - \frac{1}{2} \sum_{ss'} \beta_s^2 \beta_{s'}^2 (d_{ss'}^a - e_{ss'}^a) + \\
&\quad + \sum_s \beta_s^2 (\varepsilon_s^a (HF) - t_s^b) \ ;
\end{aligned}
\tag{36}
$$

up to higher-order contributions in β_s^2 the last term in (36) is the second-order change $-\sum_s \delta\mu_s \delta n_s$ in the energy, where $\delta\mu_s \simeq \varepsilon_s^a(HF) - t_s^b$ is the change in the chemical potential and $\delta n_s = -\beta_s^2$ is the variation of the occupation number; one may also note that the energy of the bond-like electrons as obtained from the quasi-classical treatment of the hamiltonian H_b, is of higher-order in β_s^2, so that both the last term in (26) and the last term in (36) bring quartic contributions in β_s^2, at least.

In principle, the coefficients c_{ia}^s may be determined from the purely atomic-like problem described by the energy functional E_2 given by (26), according to the standard practice of the *ab-initio* wavefunctions methods;[2] these methods provide also the atomic-type ingredients for the quantities entering the basic system of equations (19); the remaining bond-like matrix elements in (19) are given by the quasi-classical description of the bond-like electrons moving in the self-consistent potential determined by the charge distribution ρ given by (27).[6],[7] In the next step, one solves the system of equations (19) for the parameters β_s^2, and looks for a self-consistent solution for the charge density ρ (and implicitly for the parameters β_s^2). It is worth noting here that the self-consistency of this computation scheme must also satisfy the equilibrium of the atomic aggregate, *i.e.* it must be realized for the minimum value of the total energy functional E with respect to the positions of the atomic nuclei. According to this prescription the entire problem of the chemical bond as formulated here may, in principle, be solved completely. It is worth adding in this context that the quasi-classical description and the linearized Thomas-Fermi theory for the slightly inhomogeneous electron liquid formed by the bond-like electrons, as described by the effective hamiltonian H_b given by (28), lead to bound states for the atomic aggregates.[6],[7] In this scheme

of computation the atomic-like part in the energy functional E_2 given by (26) may acquire higher values than its equilibrium value corresponding to the absence of the bond-like electrons ($\beta_s^2 = 0$), as a consequence of the inter-nuclei Coulomb repulsion; the excess is, in fact, related to the condition for non-trivial solutions of equations (19), and to the existence of equilibrium, non-vanishing β_s^2-values, and, thus, to the bond-like electron dynamics; in this connection, one may also note that the last term in (26) lowers the energy E_2, in contrast to the excess of its purely atomic-like part; both the excess of the purely atomic-like contribution to E_2 and the last (β_s^2-dependent) term in E_2 acquire small values (due to the presence of the β_s^2-factors) in comparison with the purely atomic-like contribution corresponding to $\beta_s^2 = 0$; the total change in E_2 for $\beta_s^2 \neq 0$ is toward small negative values in comparison with the energy of the independent atoms, so that the binding energy of the atomic aggregate is given both by this small change in the purely atomic-like energy of the ensemble and by the energy of the bond-like electrons described by the hamiltonian H_b. However, to the first approximation, both the change in the atomic-like energy E_2 and the departure from unity of the fractional occupancy $\beta_s^2 < 1$ in the bond-like energy functional E_1 are quantum corrections within the scheme of the quasi-classical description; therefore, the binding energy of the atomic aggregate, and the chemical bond, are given, to the first approximation, solely by the hamiltonian H_b with a (formal) occupancy $\beta_s^2 = 1$.

According to the above discussion, the chemical bond is realized by electrons in the upper atomic shells contributing to the bond-like orbitals and generating the effective hamiltonian H_b given by (28); the latter, by an appropriate treatment,[6],[7] ensures the equilibrium and the stability of the atomic aggregate for certain values of the inter-nuclei distances. However, pushing the atoms closer to one another, the upper atomic shells may start to lose their identity as atomic-like orbitals, expand the width of the bands they form, while the inner shells start to be affected and develop their own energy bands; very likely, during such a process, the total electronic energy changes little, but the Coulomb repulsion between the nuclei (not included in the electronic part of the energy) increases, and opposes itself the atoms getting closer. However, passing over such a "potential barrier", and pushing the atoms close enough to one another by an external force, the energy bands formed by the inner atomic shells may contribute themselves to the bond-like orbitals, and there will be more solutions to equations (19), corresponding to more s-states participating in the chemical bond; the inner atomic shells may therefore contribute non-spontaneously to the chemical bond, through such an external force pushing the atoms closer and closer to one another; increasing the number of solutions to equations (19) results, however, in lowering the total energy, as a consequence of the action of the bond-like hamiltonian H_b (this action may simply be viewed as an increase in the effective charges z_i^*); then, one may expect another region of stability for the atomic aggregate, where the atoms are packed closer; going further on, a whole sequence of (meta-) stability regions can be obtained for atomic aggregates, characterized by tighter bonds and a closer packing, separated by high energy barriers; such regions ("islands" of meta-stability) are related to the inner atomic shells.

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[8] The diagonalization of the corresponding matrix in the atomic-like energy functional (5) with respect to the *ia*-labels represents the core of the *ab-initio* wavefunctions methods quoted in Ref. 2.