ELSES Code Overview
(CSC part)

ELSES Consortium

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Contents

Part I

Reference Manual of Charge Self-Consistency Part in ELSES

Chapter 1

Introduction to charge self-consistency

1.1 Purpose of the charge self-consistency

The main purpose of this document is explain, based on [1], the followings:

- Charge Self-Consistency (CSC) in LDA is quite straightforward. CSC in TB-formalism should be re-considered.

- To explain the necessity of CSC once we start Tight-Binding calculation.

- To formulate CSC procedure as a perturbation treatment with unperturbed Hamiltonian of the assumed TB-parameters and valence charge.

At the end of this document, several references are given. [2, 3, 4, 5]

1.2 LDA Total energy

The LDA-total energy is given as

$$E^{\text{LDA}} = \sum_i^{\text{occ}} \langle \Psi_i | -\frac{\Delta}{2} + V_{\text{ext}} + \frac{1}{2} \int dr' \frac{n'}{|\mathbf{r} - \mathbf{r}'|} |\Psi_i\rangle + E_{\text{xc}}[n] + E_{\text{ion-ion}}. \tag{1.1}$$

The density of electron is assumed to be the sum of the starting one $n^0(\mathbf{r})$ and its deviation $\delta n(\mathbf{r})$ and should be expressed as

$$\sum_i^{\text{occ}} \langle \Psi_i | \Psi_i \rangle = n(\mathbf{r}) = n^0(\mathbf{r}) + \delta n(\mathbf{r}) \tag{1.2}$$

1.3   Perturbation to starting chage distribution

1.3.1   Charge fluctuation from the starting one

All the TB-parameters are obtained with an assumption of the charge distribution $n^0(\mathbf{r})$.

Chage density of the *Reference System* : $n^0(\mathbf{r})$.

We then write the resultant density (self-consistent) as $n(\mathbf{r})$.

Let introduce the perturbation expansion of charge density starting from the TB-charge $n^0(\mathbf{r})$: *i.e.* the second term of Eq. (1.1) (the Hartree energy) is rewrirren as

$$
\begin{aligned}
&\frac{1}{2}\int\int \frac{(n^{0\prime}+\delta n')(n^0+\delta n)}{|\mathbf{r}-\mathbf{r}'|} \\
=\ &\int\int \frac{n^{0\prime}(n^0+\delta n)}{|\mathbf{r}-\mathbf{r}'|} - \frac{1}{2}\int\int \frac{n^{0\prime}(n^0+\delta n)}{|\mathbf{r}-\mathbf{r}'|} + \frac{1}{2}\int\int \frac{\delta n'(n^0+\delta n)}{|\mathbf{r}-\mathbf{r}'|} \\
=\ &\int\int \frac{n^{0\prime}(n^0+\delta n)}{|\mathbf{r}-\mathbf{r}'|} - \frac{1}{2}\int\int \frac{n^0 \prime n^0}{|\mathbf{r}-\mathbf{r}'|} + \frac{1}{2}\int\int \frac{\delta n'\delta n}{|\mathbf{r}-\mathbf{r}'|}.
\end{aligned}
\tag{1.3}
$$

Then the LDA total energy can be rewritten as

$$
\begin{aligned}
E^{\mathrm{LDA}} =\ & \sum_i^{\mathrm{occ}}\langle\Psi_i|-\frac{\Delta}{2}+V_{\mathrm{ext}}+\int d\mathbf{r}'\frac{n^{0\prime}}{|\mathbf{r}-\mathbf{r}'|}+V_{\mathrm{xc}}[n^0]|\Psi_i\rangle \\
& +E_{\mathrm{xc}}[n]-\int d\mathbf{r}V_{\mathrm{xc}}[n^0]n-\frac{1}{2}\int\int\frac{n^{0\prime}n^0}{|\mathbf{r}-\mathbf{r}'|}+\frac{1}{2}\int\int\frac{\delta n'\delta n}{|\mathbf{r}-\mathbf{r}'|}+E_{\mathrm{ion-ion}}.
\end{aligned}
\tag{1.4}
$$

Also we have the relation

$$
\begin{aligned}
E_{\mathrm{xc}}[n]-\int d\mathbf{r}V_{\mathrm{xc}}[n^0]n =\ & \left[E_{\mathrm{xc}}[n^0]+\int d\mathbf{r}V_{\mathrm{xc}}[n^0]\delta n+\frac{1}{2}\int\int d\mathbf{r}d\mathbf{r}'\frac{\delta^2 E_{\mathrm{xc}}}{\delta n\delta n'}\Big|_{n^0}\delta n\delta n'\right] \\
& -\left[\int d\mathbf{r}V_{\mathrm{xc}}[n^0]n^0+\int d\mathbf{r}V_{\mathrm{xc}}[n^0]\delta n\right] \\
=\ & E_{\mathrm{xc}}[n^0]-\int d\mathbf{r}V_{\mathrm{xc}}[n^0]n^0+\frac{1}{2}\int\int d\mathbf{r}d\mathbf{r}'\frac{\delta^2 E_{\mathrm{xc}}}{\delta n\delta n'}\Big|_{n^0}\delta n\delta n'.
\end{aligned}
\tag{1.5}
$$

Substituting Eq. (1.5) into Eq. (1.4), the LDA total energy can be written as

$$
\begin{aligned}
E^{\mathrm{LDA}} =\ & \sum_i^{\mathrm{occ}}\langle\Psi_i|-\frac{\Delta}{2}+V_{\mathrm{ext}}+\int d\mathbf{r}'\frac{n^{0\prime}}{|\mathbf{r}-\mathbf{r}'|}+V_{\mathrm{xc}}[n^0]|\Psi_i\rangle \\
& -\frac{1}{2}\int\int\frac{n^{0\prime}n^0}{|\mathbf{r}-\mathbf{r}'|}+E_{\mathrm{xc}}[n^0]-\int d\mathbf{r}V_{\mathrm{xc}}[n^0]n^0+E_{\mathrm{ion-ion}} \\
& +\frac{1}{2}\int\int d\mathbf{r}d\mathbf{r}'\frac{\delta^2 E_{\mathrm{xc}}}{\delta n\delta n'}\Big|_{n^0}\delta n\delta n'+\frac{1}{2}\int\int\frac{\delta n'\delta n}{|\mathbf{r}-\mathbf{r}'|} \\
=\ & \sum_i^{\mathrm{occ}}\langle\Psi_i|H_0|\Psi_i\rangle+E_{\mathrm{rep}}+E_{\mathrm{2nd}},
\end{aligned}
\tag{1.6}
$$

where LDA-Hamiltonian H_0, repulsive energy and 2nd order energy are

$$H_0 = -\frac{\Delta}{2} + V_{\text{ext}} + \int d\mathbf{r}' \frac{n^0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_{\text{xc}}[n^0], \tag{1.7}$$

$$E_{\text{rep}} = -\frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{n^0(\mathbf{r}) n^0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}[n^0] - \int d\mathbf{r} V_{\text{xc}}[n^0] n^0 + E_{\text{ion}-\text{ion}} \tag{1.8}$$

and

$$E_{\text{2nd}} = \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \Big[\frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta^2 E_{\text{xc}}}{\delta n \delta n'} \Big]_{n^0} \delta n(\mathbf{r}) \delta n(\mathbf{r}') \tag{1.9}$$

In the repulsive energy Eq. (1.8), the contribution by the exchange-correlation interaction (the second and the third terms) are independent on inter-atomic distances directly and, therefore, it may be not necessary to be careful much.

1.3.2   Zeroth-order energy

Assuming the resultant charge n is equal to the TB-charge n^0, then the total energy is givenm as

$$E_0^{\text{TB}} = \sum_i^{\text{occ}} \langle \Psi_i | H_0 | \Psi_i \rangle + E_{\text{rep}} = \sum_i^{\text{occ}} \varepsilon_i + E_{\text{rep}} \tag{1.10}$$

The repulsive energy is the pairwise inter-atomic potential:

$$E_{\text{rep}} = \sum_{\alpha \neq \beta} E_{\text{rep}}(|\mathbf{R}_\alpha - \mathbf{R}_\beta|) \tag{1.11}$$

The first term corresponds to the tight-binding band energy and the second-term the additional repulsive energy. This is the exact expression that the resultant charge distribution $n(\mathbf{r})$ is identical to the starting one $n^0(\mathbf{r})$, or $\delta n(\mathbf{r}) = 0$.

1.4   Second-order energy

1.4.1   Second-order energy

If the resultant cahrge $n(\mathbf{r})$ is not equal to the TB-charge $n^0(\mathbf{r})$, and it is almost always the case, we have the energy deviation (the second order energy)

$$E_{\text{2nd}} = \frac{1}{2} \sum_{\alpha\beta} \int \int d\mathbf{r} d\mathbf{r}' \Gamma[\mathbf{r}, \mathbf{r}' : n^0] \delta n(\mathbf{r}) \delta n(\mathbf{r}'), \tag{1.12}$$

which can be approximated as

$$E_{2\mathrm{nd}} = \frac{1}{2} \sum_{\alpha\beta} \Delta q_\alpha \Delta q_\beta \gamma_{\alpha\beta}, \tag{1.13}$$

where the charge fuctuation is approximated as

$$\delta n_\alpha(\mathbf{r}) \simeq \Delta q_\alpha F_{00}^\alpha(|\mathbf{r} - \mathbf{R}_\alpha|) Y_{00}(\mathbf{r} \hat{-} \mathbf{R}). \tag{1.14}$$

Generalization for orbital dependence

It must be noticed that the second-order term here is the exchange and Coulomb interactions and can be dependent upon orbital charges, since the screening process depends strongly on orbitals. In such case, we must generalize the expressions as follows:

$$\gamma_{\alpha\beta} \quad \rightarrow \quad \gamma_{\alpha\mu:\beta\nu} \tag{1.15}$$

$$q_\alpha \quad \rightarrow \quad q_{\alpha\mu}. \tag{1.16}$$

At the moment, we neglect such dependence and follow the original formulation of Elstner *et al.* [1]

1.4.2   Determining the fluctuation charge

In case we have overlap metrix in the TB formulation, the charge distribution is usually defined with a help of the Mulliken charge. Here, we assume the total charge to be given by the Mulliken formulation (Mulliken charge).

$$\begin{aligned}
q_\alpha &= \frac{1}{2} \sum_i^{\mathrm{occ}} \sum_\beta \sum_{\mu\nu} \left(c_{\alpha\mu}^{(i)*} c_{\beta\nu}^{(i)} S_{\alpha\mu:\beta\nu} + c_{\beta\nu}^{(i)*} c_{\alpha\mu}^{(i)} S_{\beta\nu:\alpha\mu} \right) \\
&= \frac{1}{2} \int^{E_f} dE \sum_\beta \sum_{\mu\nu} \left\{ G_{\alpha\mu:\beta\nu}(E) S_{\alpha\mu:\beta\nu} + G_{\beta\nu:\alpha\mu}(E) S_{\beta\nu:\alpha\mu} \right\} \\
&= \frac{1}{2} \sum_\beta \sum_{\mu\nu} \left\{ \rho_{\alpha\mu:\beta\nu} S_{\alpha\mu:\beta\nu} + \rho_{\beta\nu:\alpha\mu} S_{\beta\nu:\alpha\mu} \right\}.
\end{aligned} \tag{1.17}$$

α, β : sites
i : states (occupied)
μ, ν : orbitals
$S_{\alpha\mu:\beta\nu}$: overlap integral
$\rho_{\alpha\mu:\beta\nu}$: the diagonal and off-diagonal density matrix:

$$\rho_{\alpha\mu:\beta\nu} = \int^{E_f} dE\, G_{\alpha\mu:\beta\nu}(E) = \sum_i^{\mathrm{occ}} c_{\alpha\mu}^{(i)*} c_{\beta\nu}^{(i)} \tag{1.18}$$

$\Delta q_\alpha = q_\alpha - q_\alpha^0$, where q_α^0 is the starting charge (the TB-charge) :

$$q_\alpha = \int d\mathbf{r} n_\alpha(\mathbf{r}) \tag{1.19}$$

$$q_\alpha^0 = \int d\mathbf{r} n_\alpha^0(\mathbf{r}) \tag{1.20}$$

The Mulliken charge is reduced to the usual local charge when $S_{\alpha\mu:\beta\nu} = \delta_{\alpha\mu:\beta\nu}$.

1.5 Variational equation and forces

1.5.1 Secular equation

The eigen energies and wavefunctions are obtained by the following generallized eigen-value problem.

We write eigen-functions as a linear combination of atomic wavefunctions:

$$\Psi_i = \sum_{\alpha\mu} c_{\alpha\mu}^{(i)} \phi_{\alpha\mu}. \tag{1.21}$$

Then the seqular equation is

$$\sum_{\beta\nu} c_{\beta\nu}^{(i)} \left(H_{\alpha\mu:\beta\nu} - \varepsilon_i S_{\alpha\mu:\beta\nu} \right) = 0, \tag{1.22}$$

or more definitely

$$\sum_{\beta\nu} c_{\beta\nu}^{(i)} \left[\left\{ \langle \phi_{\alpha\mu} | H_0 | \phi_{\beta\nu} \rangle + \frac{1}{2} S_{\alpha\mu:\beta\nu} \sum_\kappa (\gamma_{\alpha\kappa} + \gamma_{\beta\kappa}) \Delta q_\kappa \right\} - \varepsilon_i S_{\alpha\mu:\beta\nu} \right] = 0. \tag{1.23}$$

Then we can define the matrix element of *effective* Hamiltonian as

$$H_{\alpha\mu:\beta\nu} = H_{\alpha\mu:\beta\nu}^{\mathrm{TB}-0} + H_{\alpha\mu:\beta\nu}^{\mathrm{CSC}}, \tag{1.24}$$

where

$$H_{\alpha\mu:\beta\nu}^{\mathrm{TB}-0} = \langle \phi_{\alpha\mu} | H_0 | \phi_{\beta\nu} \rangle, \tag{1.25}$$

$$H_{\alpha\mu:\beta\nu}^{\mathrm{CSC}} = \frac{1}{2} S_{\alpha\mu:\beta\nu} \sum_\kappa (\gamma_{\alpha\kappa} + \gamma_{\beta\kappa}) \Delta q_\kappa. \tag{1.26}$$

The first term $H_{\alpha\mu:\beta\nu}^{\mathrm{TB}-0}$ is usual TB part and the second term $H_{\alpha\mu:\beta\nu}^{\mathrm{CSC}}$ is the CSC part, which has an on-site contribution of the case $\alpha = \beta$, *i.e.* $H_{\alpha\mu:\alpha\nu}^{\mathrm{CSC}} = \delta_{\mu,\nu} \sum_\kappa \gamma_{\alpha\kappa} \Delta q_\kappa$, depending on the charge fluctuation of surrounding ions near the central atom α.

1.5.2   Forces

In a similar way, the force of the CSC formulation can be written as

$$
\begin{aligned}
\mathbf{F}_\alpha \; = \; &-\sum_i^{\text{occ}}\sum_\mu\sum_{\beta\nu} c_{\alpha\mu}^{(i)\,*} c_{\beta\nu}^{(i)}\left\{\frac{\partial(H_0)_{\alpha\mu:\beta\nu}}{\partial\mathbf{R}_\alpha} - \varepsilon_i\frac{\partial S_{\alpha\mu:\beta\nu}}{\partial\mathbf{R}_\alpha}\right\} \\
&-\sum_i^{\text{occ}}\sum_\mu\sum_{\beta\nu} c_{\beta\nu}^{(i)\,*} c_{\alpha\mu}^{(i)}\left\{\frac{\partial(H_0)_{\beta\nu:\alpha\mu}}{\partial\mathbf{R}_\alpha} - \varepsilon_i\frac{\partial S_{\beta\nu:\alpha\mu}}{\partial\mathbf{R}_\alpha}\right\} - \frac{\partial E_{\text{rep}}}{\partial\mathbf{R}_\alpha} \qquad (1.27)
\end{aligned}
$$

$$
\begin{aligned}
&-\sum_i^{\text{occ}}\sum_\mu\sum_{\beta\nu} c_{\alpha\mu}^{(i)\,*} c_{\beta\nu}^{(i)}\frac{\{\sum_\kappa(\gamma_{\alpha\kappa}+\gamma_{\beta\kappa})\Delta q_\kappa\}}{2}\frac{\partial S_{\alpha\mu:\beta\nu}}{\partial\mathbf{R}_\alpha} \\
&-\sum_i^{\text{occ}}\sum_\mu\sum_{\beta\nu} c_{\beta\nu}^{(i)\,*} c_{\alpha\mu}^{(i)}\frac{\{\sum_\kappa(\gamma_{\alpha\kappa}+\gamma_{\beta\kappa})\Delta q_\kappa\}}{2}\frac{\partial S_{\beta\nu:\alpha\mu}}{\partial\mathbf{R}_\alpha} - \Delta q_\alpha\sum_\kappa\frac{\partial\gamma_{\alpha\kappa}}{\partial\mathbf{R}_\alpha}\Delta q_\kappa
\end{aligned}
$$

$$(1.28)$$

The first and second lines, Eq. (1.27), are the usual TB-force with overlap matrix and without charge fluctuation plus the additional repulsive force. Equation (1.28) is the additional second order term due to charge fluctuation after the self-consistent calculation.

By using the density matrix Eq. (1.18)

$$
\rho_{\alpha\mu:\beta\nu} = \int^{E_f} dE\, G_{\alpha\mu:\beta\nu}(E) = \sum_i^{\text{occ}} c_{\alpha\mu}^{(i)\,*} c_{\beta\nu}^{(i)}
$$

and the energy density matrix

$$
\pi_{\alpha\mu:\beta\nu} = \int^{E_f} dE\, E\, G_{\alpha\mu:\beta\nu}(E) = \sum_i^{\text{occ}} \varepsilon_i c_{\alpha\mu}^{(i)\,*} c_{\beta\nu}^{(i)}, \qquad (1.29)
$$

the force Eqs. (1.27) and (1.28) can be rewritten as

$$
\mathbf{F}_\alpha = \mathbf{F}_\alpha^{\text{TB}-0} + \mathbf{F}_\alpha^{\text{CSC}} \qquad (1.30)
$$

where

$$
\begin{aligned}
\mathbf{F}_\alpha^{\text{TB}-0} \; = \; &-\sum_\mu\sum_{\beta\nu}\left\{\rho_{\alpha\mu:\beta\nu}\frac{\partial(H_0)_{\alpha\mu:\beta\nu}}{\partial\mathbf{R}_\alpha} - \pi_{\alpha\mu:\beta\nu}\frac{\partial S_{\alpha\mu:\beta\nu}}{\partial\mathbf{R}_\alpha}\right\} \\
&-\sum_\mu\sum_{\beta\nu}\left\{\rho_{\alpha\mu:\beta\nu}\frac{\partial(H_0)_{\beta\nu:\alpha\mu}}{\partial\mathbf{R}_\alpha} - \pi_{\alpha\mu:\beta\nu}\frac{\partial S_{\beta\nu:\alpha\mu}}{\partial\mathbf{R}_\alpha}\right\} - \frac{\partial E_{\text{rep}}}{\partial\mathbf{R}_\alpha} \quad (1.31)
\end{aligned}
$$

$$
\begin{aligned}
\mathbf{F}_\alpha^{\text{CSC}} \; = \; &-\sum_\mu\sum_{\beta\nu}\rho_{\alpha\mu:\beta\nu}\frac{\{\sum_\kappa(\gamma_{\alpha\kappa}+\gamma_{\beta\kappa})\Delta q_\kappa\}}{2}\frac{\partial S_{\alpha\mu:\beta\nu}}{\partial\mathbf{R}_\alpha} \\
&-\sum_\mu\sum_{\beta\nu}\rho_{\alpha\mu:\beta\nu}\frac{\{\sum_\kappa(\gamma_{\alpha\kappa}+\gamma_{\beta\kappa})\Delta q_\kappa\}}{2}\frac{\partial S_{\beta\nu:\alpha\mu}}{\partial\mathbf{R}_\alpha} - \Delta q_\alpha\sum_\kappa\frac{\partial\gamma_{\alpha\kappa}}{\partial\mathbf{R}_\alpha}\Delta q_\kappa
\end{aligned}
$$

$$(1.32)$$

1.5.3 $\gamma_{\alpha\beta}$-term

In order to obtain the analytic formula of the second order term Eq. (1.13), we need the form of spherical charge distribution, and we assume the form (Cf. Slater orbitals)

$$n_\alpha(r) = \frac{\tau_\alpha^3}{8\pi} \exp[-\tau_\alpha|\mathbf{r} - \mathbf{R}_\alpha|]. \tag{1.33}$$

Then, neglecting the second term (the second-derivative of the exchange-correlation) in Eq. (1.9), we should calculate the integral:

$$\gamma_{\alpha\beta} = \int d\mathbf{r} \int d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} n_\alpha(r) n_\beta(r'). \tag{1.34}$$

The result is $(R = |\mathbf{R}_\alpha - \mathbf{R}_\beta|)$

$$\gamma_{\alpha\beta} = \frac{1}{R} - \mathcal{S}(\tau_\alpha, \tau_\beta, R) \tag{1.35}$$

$$\mathcal{S}(\tau_\alpha, \tau_\beta, R) = e^{-\tau_\alpha R}\left[\frac{\tau_\beta^4 \tau_\alpha}{2(\tau_\alpha^2 - \tau_\beta^2)^2} - \frac{\tau_\beta^6 - 3\tau_\beta^4\tau_\alpha^2}{(\tau_\alpha^2 - \tau_\beta^2)^3 R}\right]$$

$$+ e^{-\tau_\beta R}\left[\frac{\tau_\alpha^4 \tau_\beta}{2(\tau_\beta^2 - \tau_\alpha^2)^2} - \frac{\tau_\alpha^6 - 3\tau_\alpha^4\tau_\beta^2}{(\tau_\beta^2 - \tau_\alpha^2)^3 R}\right]. \tag{1.36}$$

The resultant expression of $\gamma_{\alpha\alpha}$ becomes of long range type. Elstner et. al. [1] discussed that the exchange-correlation is of short range type in LDA and suggested that this term can be evaluated by using the Ewalt method in periodic systems.

In case of $\tau_\alpha = \tau_\beta$ but $\alpha \neq \beta$ The expression (1.36) should be treadted more carefully. We will rewrite (1.36) as follows:

$$\frac{2R(\tau_\alpha^2 - \tau_\beta^2)^3}{e^{-\tau_\alpha R}}\mathcal{S}(\tau_\alpha, \tau_\beta, R)$$

$$= \left[\tau_\alpha\tau_\beta^4(\tau_\alpha^2 - \tau_\beta^2)R - 2(\tau_\beta^6 - 3\tau_\beta^4\tau_\alpha^2)\right] + e^{(\tau_\alpha - \tau_\beta)R}\left[\tau_\alpha^4\tau_\beta(\tau_\alpha^2 - \tau_\beta^2)R + 2(\tau_\alpha^6 - 3\tau_\alpha^4\tau_\beta^2)\right]$$

$$= \tau_\alpha\tau_\beta^4(\tau_\alpha^2 - \tau_\beta^2)R - 2(\tau_\beta^6 - 3\tau_\beta^4\tau_\alpha^2)$$

$$+ \{1 + (\tau_\alpha - \tau_\beta)R + \frac{1}{2}(\tau_\alpha - \tau_\beta)^2 R^2 + \frac{1}{6}(\tau_\alpha - \tau_\beta)^3 R^3 + O[(\tau_\alpha - \tau_\beta)^4]\}$$

$$\times \left[\tau_\alpha^4\tau_\beta(\tau_\alpha^2 - \tau_\beta^2)R + 2(\tau_\alpha^6 - 3\tau_\alpha^4\tau_\beta^2)\right].$$

Then

$$\frac{12R(\tau_\alpha^2 - \tau_\beta^2)^3}{e^{-\tau_\alpha R}}\mathcal{S}(\tau_\alpha, \tau_\beta, R)$$

$$= 6\tau_\alpha\tau_\beta^4(\tau_\alpha^2 - \tau_\beta^2)R - 12(\tau_\beta^6 - 3\tau_\alpha^2\tau_\beta^4)$$

$$+ \{6 + 6(\tau_\alpha - \tau_\beta)R + 3(\tau_\alpha - \tau_\beta)^2 R^2 + (\tau_\alpha - \tau_\beta)^3 R^3 + O[(\tau_\alpha - \tau_\beta)^4 R^4]\}$$

$$\times \left[\tau_\alpha^4\tau_\beta(\tau_\alpha^2 - \tau_\beta^2)R + 2(\tau_\alpha^6 - 3\tau_\alpha^4\tau_\beta^2)\right]$$

$$= 12(\tau_\alpha^2 - \tau_\beta^2)^3 + 6\tau_\alpha(\tau_\alpha - \tau_\beta)^3(2\tau_\alpha^3 + 5\tau_\alpha^2\tau_\beta + 3\tau_\alpha\tau_\beta^2 + \tau_\beta^3)R$$

$$+ 6\tau_\alpha^4(\tau_\alpha - \tau_\beta)^3(\tau_\alpha + 2\tau_\beta)R^2 + \tau_\alpha^4(\tau_\alpha - \tau_\beta)^3(2\tau_\alpha^2 + 3\tau_\alpha\tau_\beta - 3\tau_\beta^2)R^3 + O[(\tau_\alpha - \tau_\beta)^4 R^4].$$

Therefore

$$
\begin{aligned}
\mathcal{S}(\tau_\alpha, \tau_\beta, R) &= \frac{e^{-\tau_\alpha R}}{R} + e^{-\tau_\alpha R}\frac{\tau_\alpha(2\tau_\alpha^3 + 5\tau_\alpha^2\tau_\beta + 3\tau_\alpha\tau_\beta^2 + \tau_\beta^3)}{2(\tau_\alpha + \tau_\beta)^3} + e^{-\tau_\alpha R}R\frac{\tau_\alpha^4(\tau_\alpha + 2\tau_\beta)}{2(\tau_\alpha + \tau_\beta)^3} \\
&\quad + e^{-\tau_\alpha R}R^2\frac{\tau_\alpha^4(2\tau_\alpha^2 + 3\tau_\alpha\tau_\beta - 3\tau_\beta^2)}{12(\tau_\alpha + \tau_\beta)^3} + O[(\tau_\alpha - \tau_\beta)e^{-\tau_\alpha R}R^3].
\end{aligned}
$$

Finally we obtain

$$
\mathcal{S}(\tau_\alpha, \tau_\alpha, R) = \frac{e^{-\tau_\alpha R}}{R}\{1 + \frac{11}{16}\tau_\alpha R + \frac{3}{16}\tau_\alpha^2 R^2 + \frac{1}{48}\tau_\alpha^3 R^3\} \qquad \cdots\cdots\cdots (*)
$$

Furthermore, using this expression,

$$
\begin{aligned}
\lim_{R\to 0}\mathcal{S}(\tau_\alpha, \tau_\alpha, R) &= \frac{1 - \tau_\alpha R + \cdots}{R}\{1 + \frac{11}{16}\tau_\alpha R + \frac{3}{16}\tau_\alpha^2 R^2 + \frac{1}{48}\tau_\alpha^3 R^3\} \\
&= \frac{1}{R} - \frac{5}{16}\tau_\alpha \qquad\qquad\qquad \cdots\cdots\cdots (**)
\end{aligned}
$$

If $\alpha = \beta$ we can get the diagonal γ parameter which may correspond to an on-ste Coulomb interaction

$$
\gamma_{\alpha\alpha} = \frac{5}{16}\tau_\alpha = U_\alpha, \tag{1.37}
$$

where U_α is the Hubbard parameter (chemical hardness) and the contribution to the total energy is

$$
\sum_\alpha \frac{1}{2}\Delta q_\alpha^2 \gamma_{\alpha\alpha}. \tag{1.38}
$$

How to determine τ_α

Since $E_{\text{2nd}} = \frac{1}{2}\sum_{\alpha\beta}\Delta q_\alpha \gamma_{\alpha\beta}\Delta q_\beta$, we can evaluate $\gamma_{\alpha\alpha}$ as

$$
\gamma_{\alpha\alpha} = \frac{5}{16}\tau_\alpha = \frac{\partial^2\Delta E_{\text{total}}}{\partial\Delta q_\alpha^2} \tag{1.39}
$$

Elstner et al. [1] calculated the derivative of the HOMO level with respect to the occupation, during the LDA self-consistent procedure, and evaluated τ_α:

$$
\gamma_{\alpha\alpha} = \frac{5}{16}\tau_\alpha = \frac{\partial\varepsilon_{\text{HOMO}}}{\partial\Delta q_\alpha}. \tag{1.40}
$$

They argued that the self-consistent LDA calculation may include somewhat the contribution of the second-order derivative of the exchange-correlation part E_{EC} in Eq. (1.13).

This term is related the coefficient of the valence charge Q in the valence orbital ionization potential VOIP in GENO package and it is just the Hubbard U term as Eq. (1.37) shows. Therefore, we can have several way to evaluate τ_α as follow:

- use Eq. (1.37) or Eq. (1.40)

- use d_1 Eq.(1.4) in GENO

- use U calculated by Constrained LDA calculation (make a table of values for several atoms

1.6 Discussion

The CSC-TB formulation is always true if we use the fixed TB-parameter set fixed in some atomic configuration.

Chapter 2

Attaching the Charge Self-Consistency (CSC) module to ELSES package

2.1 Structure of subroutines

2.1.1 calculation of Mulliken charge

- Purpose: To calculate or to get the Mulliken charge from ICON-part.

- Input:

- Output: q_α and q_α^0 in Eq. (1.17)

$$\Delta q_\alpha = q_\alpha - q_\alpha^0$$

q_α^0 may be evaluated in the Generalized Hueckel Approximation as $q_\alpha^0 = Z - Q$ and Q is the ionic charge.

2.1.2 calculation of chemical hardness τ_α and $\gamma_{\alpha\beta}$

calculation of chemical hardness τ_α

- Input:

- Output: τ_α in 1.5.3 and Eq. (1.37)

In the main part of ELSES, we should store the value of the HOMO level at each iteration step. Then we estimate the derivative of the HOMO level with respect to the occupation.

calculation of $\gamma_{\alpha\beta}$

- Input:$R = |\mathbf{R}_\alpha - \mathbf{R}_\beta|$, τ_α

- Output:$\gamma_{\alpha\beta}$ in Eq. (1.35)

2.1.3 calculation of effective Hamiltonian

- Input: $S_{\alpha\mu:\beta\nu}$, $\gamma_{\alpha\kappa}$, Δq_α

- Output:$H^{\mathrm{CSC}}_{\alpha\mu:\beta\nu}$ in Eq. (1.26)

Add the second-order term to the ICON-Hamiltonian.

2.1.4 calculation of additional terms in Force expression

- Input:$\rho_{\alpha\mu:\beta\nu}$, Δq_α, $\frac{\partial S_{\alpha\mu:\beta\nu}}{\partial \mathbf{R}_\alpha}$, $\frac{\partial \gamma_{\alpha\beta}}{\partial \mathbf{R}_\alpha}$

- Output:$\mathbf{F}^{\mathrm{CSC}}_\alpha$ in Eq. (1.32)

Add the additional tems to the force calculated in ELSES main part.
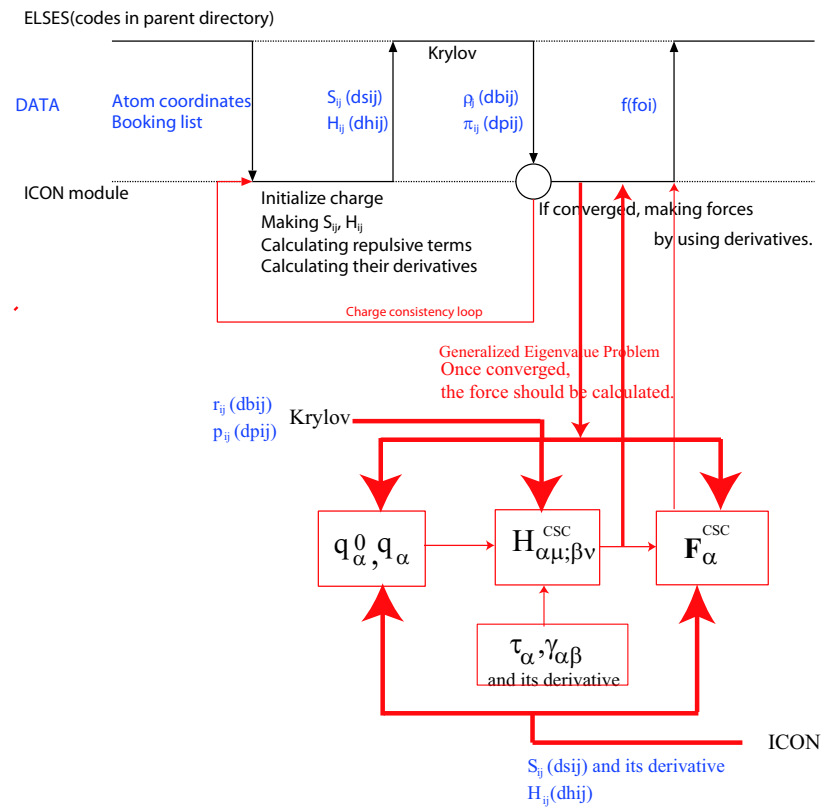
2.2 Structure of data flow

Figure 2.1: Schematic data flow of CSC calculation with ELSES and ICON.

Bibliography

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