ELSES Code Overview
(Generalized non-orthogonal base method)

ELSES Consortium

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Part I

Reference manual of GENO module in ELSES

Chapter 1

Introduction

1.1 Purpose of this module

The word GENO is a abbreviation of the "Generalized non-orthogonal base calculation". The primary purpose of this package is to generate an extended Hückel Hamiltonian and overlap matrices, similar to the ICON package. [1, 2] The explicit expression of each matrix element is given, based on the following assumptions.

- The Slater-type orbital (STO) wavefunction,

$$\phi_{nlm}^{(\text{STO},\zeta)}(\vec{r}) = R_{nl}(r)Y_l^m(\theta,\varphi), \tag{1.1}$$

$$R_{nl}(r) = \sqrt{\frac{(2\zeta)^{2n+1}}{(2n)!}} r^{n-1}\exp(-\zeta r). \tag{1.2}$$

  Here the screening parameter ζ is depending on the environment, e.g. atom species, n, and e.t.c.. [1]

  In the ELSES package, the value of ζ is supplied by the input file.

  Due to the analytic expression of the orbitals, the overlap $S_{lmn,l'm'n'}(\vec{r},\vec{r'})$ between two orbitals $\phi_{nlm}^{(\text{STO},\zeta)}(\vec{r})$ and $\phi_{n'l'm'}^{(\text{STO},\zeta')}(\vec{r'})$ is calculated analytically. [2] Its explicit expression is given in the section 1.2.1.

- We define the effective core charge Z as the number of valence electrons in the free neutral atom. And we also define the ionic charge Q as
  $Q = Z - (\text{total number of the valence electrons in the ion}).$
  Therefore, in the free neutral atom, $Q = 0$.

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[1]Cf: In the hydrogenic wavefunction, $R_{nl}(r) \sim r^l L_{n-l-1}^{2l+1}(r)\exp[-\frac{Zr}{n}]$, where L_{n-l-1}^{2l+1} denotes the associated Laguerre polynomial.

[2]This overlap is a function of ζ and ζ' too, not only of $\vec{r}$ and $\vec{r'}$

- In the present calculation, the total number of the valence electrons in the ion is calculated as Mulliken charge. Consequently,

$$Q = Z - \sum_{\substack{j,\alpha,\beta, \\ k: \text{ occupied}}} c_{i\alpha}^k c_{j\beta}^k S_{i\alpha,j\beta}, \tag{1.3}$$

where i, j denotes site, α, β denotes orbitals labeled by (n, l, m) and $c_{i\alpha}$ is a coefficient of $\phi_{nlm}^{(\text{STO},\zeta)}$ in the k-th (single electron) eigen wavefunction.

In the ELSES package, $\displaystyle\sum_{k: \text{ occupied}} c_{i\alpha}^k c_{j\beta}^k$ is given as the density matrix.

- The diagonal Hamiltonian elements are calculated by using the quadratic formula of the ionic charge Q, named as the valence orbital ionization potential (VOIP, formerly called the valence state ionization energy, VSIE) and fitted to the experiments. [3]

$$H_{ii} = - VOIP(Q)$$
$$VOIP(Q) = d_0 + d_1 Q + d_2 Q^2. \tag{1.4}$$

In the ELSES package, the values of the coefficients d_0, d_1 and d_2 are supplied by the input file.

- Wolfsberg-Helmholz formula, [4]

$$H_{ij} = K \frac{H_{ii} + H_{jj}}{2} S_{ij}, \tag{1.5}$$

where the symbol i and j denote the orbital and atom. Here, we consider the atom configuration shown in the figure (1.1).

- The correction to K, [1, 5]

$$K = 1 + (\kappa + \Delta^2 - \Delta^4 \kappa) \exp[-\delta(R - d_0)/q], \tag{1.6}$$
$$q = 1 + \{[(R - d_0) - |R - d_0|]\delta\}^2 \tag{1.7}$$

where κ and δ are positive empirical parameters (default values are $\kappa = 1.0$ and $\delta = 0.35 \mathring{A}^{-1}$) and d_0 is a sum of the orbital radii $r_n(A) + r_n(B)$. [3] The orbital radius is defined as follows;

$$\frac{1}{r_n} = \int_0^\infty \frac{1}{r} R_{nl}^2(r) r^2 \mathrm{d}r = \frac{\zeta}{n}. \tag{1.8}$$

The asymmetry between two diagonal Hamiltonian elements H_{ii} and H_{jj} is expressed with

$$\Delta = \frac{H_{ii} - H_{jj}}{H_{ii} + H_{jj}}. \tag{1.9}$$

---

[3]CAUTION: This variable is sharing the name with the constant part of the quadratic function *VOIP*.

Assuming $R = d$ and taking the limit of $|H_{jj}| = 0 (\ll |H_{ii}|, \Delta = 1)$, then one find that the correction $K = 2$ and the non-diagonal Hamiltonian element satisfies $H_{ij} = H_{ii}S_{ij}$, instead of the original $H_{ij} = \frac{1}{2}H_{ii}S_{ij}$. Thus, the Δ term is a compensation of the reduction induced by the asymmetry among two diagonal elements. [6, 1]

The R-dependence of K term is controlled to keep greater than the unity. If this constrained is omitted, the fictitious level crossing between bonding/anti-bonding states may occur. [1]

- The total energy E consists of stabilization energy ΔE_{EHMO} and the electrostatic energy E_{Rep}. Here, the suffix EHMO means "Extended Hückel Molecular Orbital". The energy E_{EHMO} is defined as the summation of single-electron energy up to the Fermi energy. The stabilization energy is defined as $\Delta E_{EHMO} = E_{EHMO} - \sum_j b_j^0 H_{jj}$, where b_j^0 is the occupation number of the atomic orbital j, in the free (neutral) atom. Consequently,

$$E_{Tot} = E_{EHMO} - \sum_j b_j^0 H_{jj} + \sum_{a,b} (E_{\text{Rep}})_{ab} \qquad (1.10)$$

- The electrostatic energy E_{Rep} is a summation of the following two-body repulsive term over all atom pairs; [8, 7]

$$(E_{\text{Rep}})_{ab} = \frac{Z_a Z_b}{R_{ab}} - \frac{Z_a}{2} \int \frac{\rho_b \mathrm{d}^3 \vec{r}}{|\vec{R}_{ab} - \vec{r}|} - \frac{Z_b}{2} \int \frac{\rho_a \mathrm{d}^3 \vec{r}}{|\vec{R}_{ab} - \vec{r}|}, \qquad (1.11)$$

where the ρ_a is a electron density on the atom A. The explicit expression of this term is given in the section 1.2.4

1.2 Explicit expressions of related matrices

1.2.1 Analytic expression of overlap between two STO's

The overlap integral between two STO's depends on the direction cosine as in the famous Slater-Koster table. Then we must calculate $S_{ss\sigma}$, $S_{sp\sigma}$, $S_{pp\sigma}$, $S_{pp\pi}$, ... , $S_{l_a l_b m}$, ... They are calculated at the special atom configuration, such that direction cosine is equal to $(0, 0, 1)$. This configuration is shown in figure (1.1), and, we use this atom layout to calculate $S_{l_a l_b m}$ in the present section.
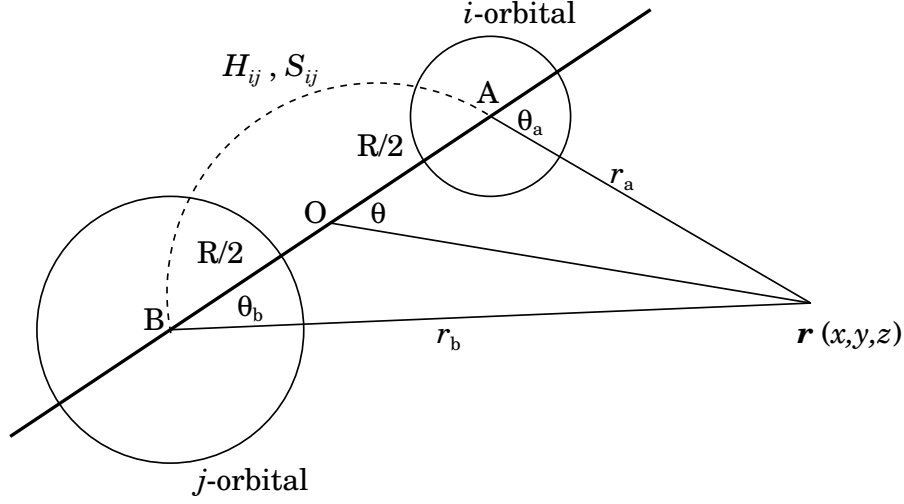
Figure 1.1: The atom layout.

Prolate spheroidal coordinate

The diagonal elements are equal to the unity, apparently. The non-diagonal matrix element between arbitrary pair of the two orbitals represented as

$$
\int_0^\infty r^2 \mathrm{d}r \int_0^\pi \sin\theta \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\varphi
$$

$$
\sqrt{\frac{(2\zeta_b)^{2n_b+1}}{(2n_b)!}} \sqrt{\frac{(l_b-m_b)!(2l_b+1)}{2(l_b+m_b)!}} r_b^{n_b-1} \mathrm{e}^{-\zeta_b r_b} P_{l_b}^{m_b}(\cos\theta_b) \frac{\mathrm{e}^{-\mathrm{i}m_b\varphi}}{\sqrt{2\pi}}
$$

$$
\sqrt{\frac{(2\zeta_a)^{2n_a+1}}{(2n_a)!}} \sqrt{\frac{(l_a-m_a)!(2l_a+1)}{2(l_a+m_a)!}} r_a^{n_a-1} \mathrm{e}^{-\zeta_a r_a} P_{l_a}^{m_a}(\cos\theta_a) \frac{\mathrm{e}^{\mathrm{i}m_a\varphi}}{\sqrt{2\pi}}, \tag{1.12}
$$

where the $P_l^m(x)$ is an associated Legendre function. The configuration of the respective atoms are shown in the figure (1.1). We obtain the analytic expression of above integral, taking advantage of the prolate spheroidal coordinate

$$
x = \frac{R}{2}\sinh\Theta\sin\Phi\cos\varphi, \tag{1.13}
$$

$$
y = \frac{R}{2}\sinh\Theta\sin\Phi\sin\varphi, \tag{1.14}
$$

$$
z = \frac{R}{2}\cosh\Theta\cos\Phi. \tag{1.15}
$$
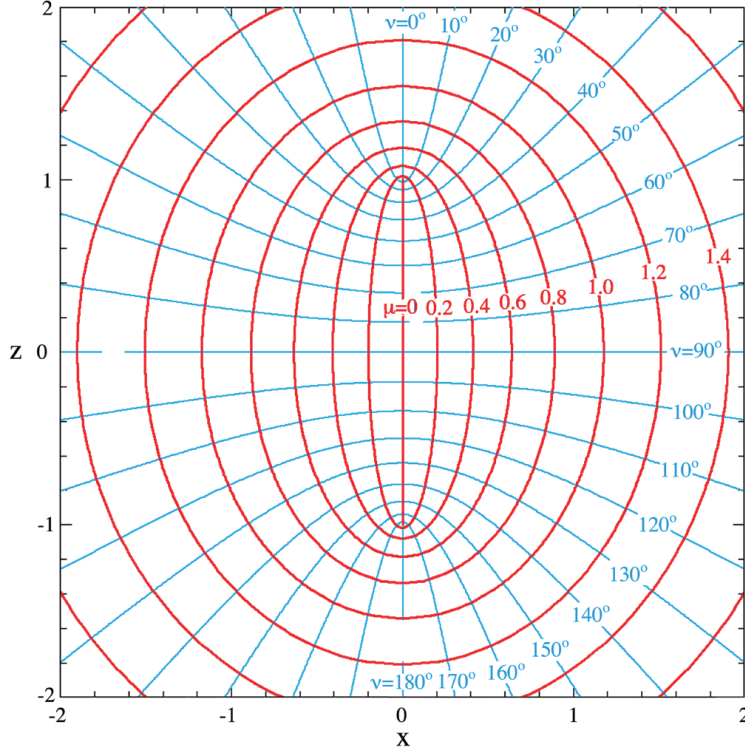
Figure 1.2: The prolate spheroidal coordinate system ($R = 2, \varphi = 0$). This public domain figure is imported from the Wikipedia.[9] The notation in the figure is different from the text. Ths symbol μ and ν in the figure stands for the Θ and Φ in the text, respectively.

One easily confirm that the prolate spheroidal coordinate (Θ, Φ, φ) is a orthogonal coordinate system. In addition to that, this coordinate system satisfiles following relation,

$$\frac{z^2}{\left(\frac{R}{2}\right)^2 \cosh^2 \Theta} + \frac{x^2 + y^2}{\left(\frac{R}{2}\right)^2 \sinh^2 \Theta} = 1, \tag{1.16}$$

$$\frac{z^2}{\left(\frac{R}{2}\right)^2 \cos^2 \Phi} - \frac{x^2 + y^2}{\left(\frac{R}{2}\right)^2 \sin^2 \Phi} = 1. \tag{1.17}$$

Therefore, the curve $\Theta = 0$ appears as elliptic one and the curve $\Phi = 0$ appears as hyperbolic one in zx- or yz-plane, sharing the forci A and B in the figure 1.1.

For the convenience, we define μ and ν as $\mu = \cosh\Theta$ and $\nu = \cos\Phi$, then we obtain

$$r_a = \frac{R}{2}(\mu - \nu), \tag{1.18}$$

$$r_b = \frac{R}{2}(\mu + \nu), \tag{1.19}$$

$$dv = (\frac{R}{2})^3(\mu^2 - \nu^2)d\mu d\nu d\varphi, \tag{1.20}$$

$$\cos\theta_a = \frac{\mu\nu - 1}{\mu - \nu}, \tag{1.21}$$

$$\cos\theta_b = \frac{\mu\nu + 1}{\mu + \nu}. \tag{1.22}$$

Then, the non-diagonal overlap matrix element is represented as

$$\text{(normalizing factors)}(\frac{R}{2})^{n_a+n_b+1}\delta_{m_a m_b}\int_1^\infty d\mu \int_{-1}^1 d\nu$$
$$(\mu - \nu)^{n_a} P_{l_a}^m(\frac{\mu\nu - 1}{\mu - \nu})(\mu + \nu)^{n_b} P_{l_b}^m(\frac{\mu\nu + 1}{\mu + \nu})e^{-\frac{R}{2}[(\zeta_a+\zeta_b)\mu+(\zeta_a-\zeta_b)\nu]}, \tag{1.23}$$

where $m = m_a = m_b \geq 0$. For the negative m, use the relation $P_l^{-m}(x) = (-1)^{-m}\frac{(l-m)!}{(l+m)!}P_l^m(x)$.

Because $P_l^m(x) = \frac{(-1)^m}{2^l l!}(1 - x^2)^{\frac{m}{2}}(\frac{d}{dx})^{l+m}(x^2 - 1)^l$,

$$(\mu \mp \nu)^n P_l^m(\frac{\mu\nu \mp 1}{\mu \mp \nu}) = \frac{1}{2^l l!}\left(\sqrt{\frac{(\mu^2 - 1)(1 - \nu^2)}{\mu^2 - \nu^2}}\right)^m$$
$$\sum_{j=0}^{\lfloor\frac{l-m}{2}\rfloor}\binom{l}{j}\frac{[2(l - j)]!}{(l - m - 2j)!}(\mu\nu \mp 1)^{l-m-2j}(\mu \mp \nu)^{n-(l-m-2j)}(-1)^{m+j}. \tag{1.24}$$

Then the integrand in the eq. (1.23) is equal to

$$(\mu - \nu)^{n_a} P_{l_a}^m (\frac{\mu\nu - 1}{\mu - \nu})(\mu + \nu)^{n_b} P_{l_b}^m (\frac{\mu\nu + 1}{\mu + \nu})e^{-\frac{R}{2}[(\zeta_a + \zeta_b)\mu + (\zeta_a - \zeta_b)\nu]}$$

$$=\frac{(\mu^2 - 1)^m (1 - \nu^2)^m}{2^{l_a} l_a! 2^{l_b} l_b!} \sum_{j_a=0}^{\lfloor \frac{l_a - m}{2} \rfloor} \sum_{j_b=0}^{\lfloor \frac{l_b - m}{2} \rfloor} \binom{l_a}{j_a} \frac{[2(l_a - j_a)]!}{(l_a - m - 2j_a)!} \binom{l_b}{j_b} \frac{[2(l_b - j_b)]!}{(l_b - m - 2j_b)!}$$

$$(\mu\nu - 1)^{l_a - m - 2j_a}(\mu\nu + 1)^{l_b - m - 2j_b}(\mu - \nu)^{n_a - l_a + 2j_a}(\mu + \nu)^{n_b - l_b + 2j_b}(-1)^{j_a + j_b}$$

$$e^{-\frac{R}{2}[(\zeta_a + \zeta_b)\mu + (\zeta_a - \zeta_b)\nu]}$$

$$=\frac{1}{2^{l_a} l_a! 2^{l_b} l_b!} \sum_{j_a=0}^{\lfloor \frac{l_a - m}{2} \rfloor} \sum_{p_a=0}^{l_a - m - 2j_a} \sum_{q_a=0}^{n_a - l_a + 2j_a} \sum_{j_b=0}^{\lfloor \frac{l_b - m}{2} \rfloor} \sum_{p_b=0}^{l_b - m - 2j_b} \sum_{q_b=0}^{n_b - l_b + 2j_b} \sum_{k=0}^{m} \sum_{k'=0}^{m}$$

$$\binom{l_a}{j_a} \frac{[2(l_a - j_a)]!}{(l_a - m - 2j_a)!} \binom{l_a - m - 2j_a}{p_a} \binom{n_a - l_a + 2j_a}{q_a}$$

$$\binom{l_b}{j_b} \frac{[2(l_b - j_b)]!}{(l_b - m - 2j_b)!} \binom{l_b - m - 2j_b}{p_b} \binom{n_b - l_b + 2j_b}{q_b}$$

$$\binom{m}{k}\binom{m}{k'}\mu^{(l_a - m - 2j_a - p_a) + (l_b - m - 2j_b - p_b) + (n_a - l_a + 2j_a - q_a) + (n_b - l_b + 2j_b - q_b) + 2(m-k)}$$

$$\nu^{(l_a - m - 2j_a - p_a) + (l_b - m - 2j_b - p_b) + q_a + q_b + 2(m-k')}(-1)^{p_a + q_a + j_a + j_b + k + k' + m}$$

$$e^{-\frac{R}{2}(\zeta_a + \zeta_b)\mu}e^{-\frac{R}{2}(\zeta_a - \zeta_b)\nu}. \tag{1.25}$$

Here, we easily confirm following facts.

- The integrand has a two factor. One of them is a polynomial of μ and ν. The other is an exponential function of μ and ν.

- Each term in the above summation is factorized as (μ-integral) × (ν-integral).

Finally, under the condition that $\vec{r}_a = \vec{r}_b + R_{ab}(0, 0, 1)^T$ (in Cartesian coordinate system),

the explicit expression of the overlap matrix element is

$$S_{n_b l_b m_b, n_a l_a m_a}(\vec{r}_b, \vec{r}_a) = \langle \phi_{n_b l_b m_b}(\vec{r} - \vec{r}_b) | \varphi_{n_a l_a m_a}(\vec{r} - \vec{r}_a) \rangle$$

$$= \delta_{m_a, m_b} \left(\frac{R}{2}\right)^{n_a + n_b + 1} \sqrt{\frac{(2\zeta_a)^{2n_a+1}}{(2n_a)!} \frac{(2\zeta_b)^{2n_b+1}}{(2n_b)!}} \sqrt{\frac{(l_a - m)!(2l_a + 1)}{2(l_a + m)!} \frac{(l_b - m)!(2l_b + 1)}{2(l_b + m)!}}$$

$$\frac{1}{2^{l_a} l_a! 2^{l_b} l_b!} \sum_{j_a=0}^{\lfloor \frac{l_a - m}{2} \rfloor} \sum_{p_a=0}^{l_a - m - 2j_a} \sum_{q_a=0}^{n_a - l_a + 2j_a} \sum_{j_b=0}^{\lfloor \frac{l_b - m}{2} \rfloor} \sum_{p_b=0}^{l_b - m - 2j_b} \sum_{q_b=0}^{n_b - l_b + 2j_b} \sum_{k=0}^{m} \sum_{k'=0}^{m}$$

$$\binom{l_a}{j_a} \frac{[2(l_a - j_a)]!}{(l_a - m - 2j_a)!} \binom{l_a - m - 2j_a}{p_a} \binom{n_a - l_a + 2j_a}{q_a}$$

$$\binom{l_b}{j_b} \frac{[2(l_b - j_b)]!}{(l_b - m - 2j_b)!} \binom{l_b - m - 2j_b}{p_b} \binom{n_b - l_b + 2j_b}{q_b}$$

$$\binom{m}{k} \binom{m}{k'} (-1)^{p_a + q_a + j_a + j_b + k + k' + m}$$

$$A(n_a + n_b - p_a - p_b - q_a - q_b - 2k, \frac{R}{2}(\zeta_a + \zeta_b))$$

$$B(l_a + l_b - p_a - p_b + q_a + q_b - 2(j_a + j_b + k'), \frac{R}{2}(\zeta_a - \zeta_b)), \tag{1.26}$$

where A and B are the μ- and ν-integral respectively, and defined as

$$A(n, \lambda) = \int_1^\infty x^n e^{-\lambda x} dx, \tag{1.27}$$

$$B(n, \lambda) = \int_{-1}^1 x^n e^{-\lambda x} dx. \tag{1.28}$$

Analytic properties of A and B function

Once we define the integral I, [4]

$$I(n, \lambda, t) = \left(-\frac{\partial}{\partial \lambda}\right)^n \int_t^\infty e^{-\lambda x} dx = \left(-\frac{\partial}{\partial \lambda}\right)^n \frac{e^{-\lambda t}}{\lambda} = e^{-\lambda t} \sum_{k=0}^n \frac{n!}{(n-k)!} \frac{t^{n-k}}{\lambda^{k+1}}$$

$$= \frac{n!}{\lambda^{n+1}} e^{-\lambda t} \sum_{k=0}^n \frac{(\lambda t)^k}{k!}, \tag{1.29}$$

then A and B functions are expressed as

$$A(n, \lambda) = I(n, \lambda, 1), \tag{1.30}$$

$$B(n, \lambda) = I(n, \lambda, -1) - I(n, \lambda, 1), \tag{1.31}$$

---

[4]This integral is related to the famous incomplete gamma function $\Gamma(a, x) = \int_x^\infty t^{a-1} e^{-t} dt$, through the following relation $I(n, \lambda, t) = \frac{\Gamma(n+1, \lambda t)}{\lambda^{n+1}}$.

for positive λ.

The negative λ or $\lambda = 0$ is solely required in the calculation of B function. Though $I(n, \lambda, t)$ diverges in the region of $\Re(\lambda) \leq 0$, this singularity cancels out in the B function. To show this cancellation, it is convenient to use Laurent expansion of the integral I.

$$
I(n, \lambda, t) = \left(-\frac{\partial}{\partial \lambda}\right)^n \frac{e^{-\lambda t}}{\lambda} = \left(-\frac{\partial}{\partial \lambda}\right)^n \left(\frac{1}{\lambda} - t \sum_{k=0}^{\infty} \frac{(-t\lambda)^k}{(k+1)!}\right)
$$
$$
= \frac{n!}{\lambda^{n+1}} - t^{n+1} \sum_{k=0}^{\infty} \frac{(-t\lambda)^k}{(k+n+1)k!}. \tag{1.32}
$$

This leads to

$$
B(n, \lambda) = \lim_{t \to 1}[I(n, \lambda, -t) - I(n, \lambda, t)] = \sum_{k=0}^{\infty} \frac{(-1)^n + (-1)^k}{(k+n+1)k!} \lambda^k. \tag{1.33}
$$

In this expression $\lambda^0 = 1$, for convenience. Now, we obtain the value of B function at $\lambda = 0$,

$$
B(n, 0) = \begin{cases} \frac{2}{n+1}, & \text{for even } n \\ 0, & \text{otherwise} \end{cases}. \tag{1.34}
$$

This expression is, of course, consistent with the direct integration of the eq. (1.28) under the condition $\lambda = 0$.

Summary of this subsection: Explicit expressions of A and B functions

The A and B functions are expressed by the integral I, and, the analytic expression of I has two form,

$$
I(n, \lambda, t) = n! e^{-\lambda t} \sum_{k=0}^{n} \frac{t^k}{k! \lambda^{n+1-k}}, \tag{1.35}
$$

$$
I(n, \lambda, t) = \frac{n!}{\lambda^{n+1}} - t^{n+1} \sum_{k=0}^{\infty} \frac{(-t\lambda)^k}{(k+n+1)k!}. \tag{1.36}
$$

The former expression eq. (1.35) is a finite summation but the cancellation error may be serious when $|\lambda|$ is small and the $t\lambda < 0$, due to alternating sign of the inverse series of λ. The latter expression eq. (1.36) is a infinite series but has the separate contribution of the pole at $\lambda = 0$.

In the calculation of A function, λ is always positive and $t = 1$, then the every term in eq. (1.35) is positive and no cancellation error occurs. Consequently, eq. (1.35) is suitable for numerical calculation of A function, because that is expressed as a finite summation. However, in the calculation of B function, we must take the difference between $I(n, \lambda, t)$ and $I(n, \lambda, -t)$, such as the two contributions of respective pole cancels out. Therefore,

eq. (1.35) may causes serious cancellation error problem. Then, the analytic expression eq. (1.36) or (1.33) is preferable for numerical calculation, though the original ICON code does not use this expression eq. (1.33). In addition to that, the derivative of B function has rather simple expression.

In conclusion, the explicit expressions of A and B functions and their derivatives, which is required to calculate the force, are

$$A(n, \lambda) = n! e^{-\lambda} \sum_{k=0}^{n} \frac{1}{(n-k)! \lambda^{k+1}}, \tag{1.37}$$

$$B(n, \lambda) = \begin{cases} 2 \sum_{m=0}^{\infty} \frac{\lambda^{2m}}{(n+2m+1)(2m)!}, & \text{for even } n \\ -2 \sum_{m=0}^{\infty} \frac{\lambda^{2m+1}}{(n+2m+2)(2m+1)!}, & \text{otherwise} \end{cases}, \tag{1.38}$$

$$\frac{\partial}{\partial \lambda} A(n, \lambda) = -n! e^{-\lambda} \sum_{k=0}^{n} \frac{1}{(n-k)! \lambda^{k+1}} \frac{\lambda+k+1}{\lambda}, \tag{1.39}$$

$$\frac{\partial}{\partial \lambda} B(n, \lambda) = \begin{cases} 2 \sum_{m=0}^{\infty} \frac{\lambda^{2m+1}}{(n+2m+3)(2m+1)!}, & \text{for even } n \\ -2 \sum_{m=0}^{\infty} \frac{\lambda^{2m}}{(n+2m+2)(2m)!}, & \text{otherwise} \end{cases}. \tag{1.40}$$

1.2.2 Slater-Koster table

Slater-Koster coefficients and their derivatives for each coordinate (x, y, z) are required to calculate quantum mechanical force. In the NRL part of ELSES package, they are calculated by the functions in the module "sktable" (Slater-Koster coefficient) and in the functions in the "skderiv". These modules are located in "Nrl/sktable.f90" and "Nrl/skderiv.f90", respectively.

Explicit expressions are cited from the unpublished document, written by Dr. Iguchi, related to his dissertation. One must take care about following two issues in order to correctly interpret these expressions.

- Three elements of every column vector show their x-, y-, z-component, from top row to the bottom row.

- In the actual calculations, $V_{ll'm}$'s ($V_{ss\sigma}$, $V_{sp\sigma}$,...) are dependent on r, but in the following expressions, r-dependence is omitted. Therefore, in order to obtain full derivative, one must augment the r-derivatives of $V_{ll'm}$'s. For example, the derivative of $V_{s,x}$ is expressed as $r \dfrac{\partial V_{s,x}}{\partial \vec{r}} = \begin{pmatrix} (-l^2+1)V_{sp\sigma} \\ -lmV_{sp\sigma} \\ -lnV_{sp\sigma} \end{pmatrix}$, bellow.

But the actual form is $\dfrac{\partial V_{s,x}}{\partial \vec{r}} = \dfrac{V_{sp\sigma}}{r} \begin{pmatrix} -l^2 + 1 \\ -lm \\ -ln \end{pmatrix} + l\dfrac{\partial V_{sp\sigma}}{\partial r} \begin{pmatrix} l \\ m \\ n \end{pmatrix}$. One should be noticed that the factor $l\frac{\partial V_{sp\sigma}}{\partial r}$ in the second term of this expression is calculated by using the subroutine skderive, replacing $V_{s,x}$ with $\frac{\partial V_{sp\sigma}}{\partial r}$ in the eq. (1.41).

s-s interaction

Slater-Koster coefficients of s-s interaction are

$$V_{s,s} = V_{ss\sigma}$$

The derivative of the Slater-Koster coefficients is zero when potential parameter is fixed.

s-p interaction

Slater-Koster coefficients of s-p interaction are

$$V_{s,x} = lV_{sp\sigma} \tag{1.41}$$

The derivative of the Slater-Koster coefficients with potential parameters fixed are

$$r\frac{\partial V_{s,x}}{\partial \vec{r}} = \begin{pmatrix} (-l^2 + 1)V_{sp\sigma} \\ -lmV_{sp\sigma} \\ -lnV_{sp\sigma} \end{pmatrix}$$

p-p interaction

V_{pp1} and V_{pp2} are defined as

$$V_{pp1} = V_{pp\sigma} - V_{pp\pi}$$
$$V_{pp2} = V_{pp\pi}$$

Slater-Koster coefficients of p-p interaction are

$$V_{x,x} = l^2 V_{pp1} + V_{pp2}$$
$$V_{x,y} = lmV_{pp1}$$
$$V_{x,z} = lnV_{pp1}$$

The derivative of the Slater-Koster coefficients with potential parameters fixed are

$$r\frac{\partial V_{x,x}}{\partial \vec{r}} = \begin{pmatrix} 2l(-l^2 + 1)V_{pp1} \\ -2l^2 mV_{pp1} \\ -2l^2 nV_{pp1} \end{pmatrix}$$

$$r\frac{\partial V_{x,y}}{\partial \vec{r}} = \begin{pmatrix} m(-2l^2 + 1)V_{pp1} \\ l(-2m^2 + 1)V_{pp1} \\ -2lmnV_{pp1} \end{pmatrix}$$

$$r\frac{\partial V_{x,z}}{\partial \vec{r}} = \begin{pmatrix} n(-2l^2+1)V_{pp1} \\ -2lmnV_{pp1} \\ l(-2n^2+1)V_{pp1} \end{pmatrix}$$

s-d interaction

Slater-Koster coefficients of s-d interaction are

$$V_{s,xy} = \sqrt{3}lmV_{sd\sigma}$$

$$V_{s,x^2-y^2} = \frac{\sqrt{3}}{2}(l^2-m^2)V_{sd\sigma}$$

$$V_{s,3z^2-r^2} = \frac{1}{2}(3n^2-1)V_{sd\sigma}$$

The derivative of the Slater-Koster coefficients with potential parameters fixed are

$$r\frac{\partial V_{s,xy}}{\partial \vec{r}} = \begin{pmatrix} \sqrt{3}m(-2l^2+1)V_{sd\sigma} \\ \sqrt{3}l(-2m^2+1)V_{sd\sigma} \\ \sqrt{3}(-2lmn)V_{sd\sigma} \end{pmatrix}$$

$$r\frac{\partial V_{s,x^2-y^2}}{\partial \vec{r}} = \begin{pmatrix} \sqrt{3}l(-l^2+m^2+1)V_{sd\sigma} \\ \sqrt{3}m(-l^2+m^2-1)V_{sd\sigma} \\ \sqrt{3}n(-l^2+m^2)V_{sd\sigma} \end{pmatrix}$$

$$r\frac{\partial V_{s,3z^2-r^2}}{\partial \vec{r}} = \begin{pmatrix} -3ln^2V_{sd\sigma} \\ -3mn^2V_{sd\sigma} \\ 3n(-n^2+1)V_{sd\sigma} \end{pmatrix}$$

p-d interaction

V_{pd1} and V_{pd2} are defined as

$$V_{pd1} = \sqrt{3}V_{pd\sigma} - 2V_{pd\pi}$$
$$V_{pd2} = V_{pd\pi}$$

Slater-Koster coefficients of p-d interaction are

$$V_{x,xy} = m(l^2V_{pd1} + V_{pd2})$$
$$V_{y,xy} = l(m^2V_{pd1} + V_{pd2})$$
$$V_{z,xy} = lmnV_{pd1}$$
$$V_{x,x^2-y^2} = \frac{1}{2}l\{(l^2-m^2)V_{pd1} + V_{pd2}\}$$
$$V_{y,x^2-y^2} = \frac{1}{2}m\{(l^2-m^2)V_{pd1} - V_{pd2}\}$$
$$V_{z,x^2-y^2} = \frac{1}{2}n(l^2-m^2)V_{pd1}$$

$$V_{x,3z^2-r^2} = \frac{1}{\sqrt{3}} l\{(3n^2 - 1)V_{pd1} - 2V_{pd2}\}$$

$$V_{y,3z^2-r^2} = \frac{1}{\sqrt{3}} m\{(3n^2 - 1)V_{pd1} - 2V_{pd2}\}$$

$$V_{z,3z^2-r^2} = \frac{1}{\sqrt{3}} n\{(3n^2 - 1)V_{pd1} + 4V_{pd2}\}$$

Then, the derivative of the Slater-Koster coefficients with potential parameters fixed are as follows:

$$r\frac{\partial V_{x,xy}}{\partial \vec{r}} = \begin{pmatrix} lm\{(-3l^2 + 2)V_{pd1} - V_{pd2}\} \\ l^2(-3m^2 + 1)V_{pd1} + (1 - m^2)V_{pd2} \\ mn(-3l^2 V_{pd1} - V_{pd2}) \end{pmatrix}$$

$$r\frac{\partial V_{y,xy}}{\partial \vec{r}} = \begin{pmatrix} m^2(-3l^2 + 1)V_{pd1} + (1 - l^2)V_{pd2} \\ lm\{(-3m^2 + 2)V_{pd1} - V_{pd2}\} \\ ln(-3m^2 V_{pd1} - V_{pd2}) \end{pmatrix}$$

$$r\frac{\partial V_{z,xy}}{\partial \vec{r}} = \begin{pmatrix} mn(-3l^2 + 1)V_{pd1} \\ ln(-3m^2 + 1)V_{pd1} \\ lm(-3n^2 + 1)V_{pd1} \end{pmatrix}$$

$$r\frac{\partial V_{x,x^2-y^2}}{\partial \vec{r}} = \begin{pmatrix} \frac{1}{2}\{3l^2(-l^2 + m^2 + 1) - m^2\}V_{pd1} + (-l^2 + 1)V_{pd2} \\ lm\{\frac{1}{2}(-3l^2 + 3m^2 - 2)V_{pd1} - V_{pd2}\} \\ ln\{\frac{3}{2}(-l^2 + m^2)V_{pd1} - V_{pd2}\} \end{pmatrix}$$

$$r\frac{\partial V_{y,x^2-y^2}}{\partial \vec{r}} = \begin{pmatrix} lm\{\frac{1}{2}(-3l^2 + 3m^2 + 2)V_{pd1} + V_{pd2}\} \\ \frac{1}{2}\{3m^2(-l^2 + m^2 - 1) + l^2\}V_{pd1} + (m^2 - 1)V_{pd2} \\ mn\{\frac{3}{2}(-l^2 + m^2)V_{pd1} + V_{pd2}\} \end{pmatrix}$$

$$r\frac{\partial V_{z,x^2-y^2}}{\partial \vec{r}} = \begin{pmatrix} \frac{1}{2}ln(-3l^2 + 3m^2 + 2)V_{pd1} \\ \frac{1}{2}mn(-3l^2 + 3m^2 - 2)V_{pd1} \\ \frac{1}{2}(l^2 - m^2)(-3n^2 + 1)V_{pd1} \end{pmatrix}$$

$$r\frac{\partial V_{x,3z^2-r^2}}{\partial \vec{r}} = \begin{pmatrix} \frac{1}{2\sqrt{3}}[\{(-3l^2 + 1)(3n^2 - 1) - 2l^2\}V_{pd1} + 2(l^2 - 1)V_{pd2}] \\ \frac{1}{2\sqrt{3}}lm\{(-9n^2 + 1)V_{pd1} + 2V_{pd2}\} \\ \frac{1}{2\sqrt{3}}ln\{(-9n^2 + 7)V_{pd1} + 2V_{pd2}\} \end{pmatrix}$$

$$r\frac{\partial V_{y,3z^2-r^2}}{\partial \vec{r}} = \begin{pmatrix} \frac{1}{2\sqrt{3}}lm\{(-9n^2 + 1)V_{pd1} + 2V_{pd2}\} \\ \frac{1}{2\sqrt{3}}[\{(-3m^2 + 1)(3n^2 - 1) - 2m^2\}V_{pd1} + 2(m^2 - 1)V_{pd2}] \\ \frac{1}{2\sqrt{3}}mn\{(-9n^2 + 7)V_{pd1} + 2V_{pd2}\} \end{pmatrix}$$

$$r\frac{\partial V_{z,3z^2-r^2}}{\partial \vec{r}} = \begin{pmatrix} \frac{1}{2\sqrt{3}}ln\{(-9n^2 + 1)V_{pd1} - 4V_{pd2}\} \\ \frac{1}{2\sqrt{3}}mn\{(-9n^2 + 1)V_{pd1} - 4V_{pd2}\} \\ \frac{1}{2\sqrt{3}}[\{-(-3n^2 + 1)^2 + 4n^2\}V_{pd1} + 4(1 - n^2)V_{pd2}] \end{pmatrix}$$

d-d interaction

V_{dd1}, V_{dd2}, and V_{dd3} are defined as

$$
\begin{aligned}
V_{dd1} &= 3V_{dd\sigma} - 4V_{dd\pi} + V_{dd\delta} \\
V_{dd2} &= V_{dd\pi} - V_{dd\delta} \\
V_{dd3} &= V_{dd\delta}
\end{aligned}
$$

Slater-Koster coefficients of d-d interaction are as follows

$$
\begin{aligned}
V_{xy,xy} &= l^2 m^2 V_{dd1} + (1 - n^2)V_{dd2} + V_{dd3} \\
V_{xy,yz} &= lm^2 n V_{dd1} + ln V_{dd2} \\
V_{xy,zx} &= l^2 mn V_{dd1} + mn V_{dd2} \\
V_{xy,x^2-y^2} &= \frac{1}{2} lm(l^2 - m^2)V_{dd1} \\
V_{yz,x^2-y^2} &= \frac{1}{2} mn\{(l^2 - m^2)V_{dd1} - 2V_{dd2}\} \\
V_{zx,x^2-y^2} &= \frac{1}{2} ln\{(l^2 - m^2)V_{dd1} + 2V_{dd2}\} \\
V_{xy,3z^2-r^2} &= \frac{1}{2\sqrt{3}} lm\{(3n^2 - 1)V_{dd1} - 4V_{dd2}\} \\
V_{yz,3z^2-r^2} &= \frac{1}{2\sqrt{3}} mn\{(3n^2 - 1)V_{dd1} + 2V_{dd2}\} \\
V_{zx,3z^2-r^2} &= \frac{1}{2\sqrt{3}} ln\{(3n^2 - 1)V_{dd1} + 2V_{dd2}\} \\
V_{x^2-y^2,x^2-y^2} &= \frac{1}{4}(l^2 - m^2)^2 V_{dd1} + (1 - n^2)V_{dd2} + V_{dd3} \\
V_{x^2-y^2,3z^2-r^2} &= \frac{1}{4\sqrt{3}}(l^2 - m^2)\{(3n^2 - 1)V_{dd1} - 4V_{dd2}\} \\
V_{3z^2-r^2,3z^2-r^2} &= \frac{1}{12}(3n^2 - 1)^2 V_{dd1} + \frac{1}{3}(3n^2 + 1)V_{dd2} + V_{dd3}
\end{aligned}
$$

Then, the derivative of Slater-Koster coefficients are as follows:

$$
r\frac{\partial V_{xy,xy}}{\partial \vec{r}} = \begin{pmatrix} 2l\{m^2(-2l^2 + 1)V_{dd1} + n^2 V_{dd2}\} \\ 2m\{l^2(-2m^2 + 1)V_{dd1} + n^2 V_{dd2}\} \\ 2n\{-2l^2 m^2 V_{dd1} + (n^2 - 1)V_{dd2}\} \end{pmatrix}
$$

$$
r\frac{\partial V_{xy,yz}}{\partial \vec{r}} = \begin{pmatrix} n\{m^2(-4l^2 + 1)V_{dd1} + (-2l^2 + 1)V_{dd2}\} \\ 2lmn\{(-2m^2 + 1)V_{dd1} - V_{dd2}\} \\ l\{m^2(-4n^2 + 1)V_{dd1} + (-2n^2 + 1)V_{dd2}\} \end{pmatrix}
$$

$$
r\frac{\partial V_{xy,zx}}{\partial \vec{r}} = \begin{pmatrix} 2lmn\{(-2l^2 + 1)V_{dd1} - V_{dd2}\} \\ n\{l^2(-4m^2 + 1)V_{dd1} + (-2m^2 + 1)V_{dd2}\} \\ m\{l^2(-4n^2 + 1)V_{dd1} + (-2n^2 + 1)V_{dd2}\} \end{pmatrix}
$$

$$r\frac{\partial V_{xy,x^2-y^2}}{\partial \vec{r}} = \begin{pmatrix} \frac{1}{2}m\{(l^2-m^2)(-4l^2+1)+2l^2\}V_{dd1}\} \\ \frac{1}{2}l\{(l^2-m^2)(-4m^2+1)+2m^2\}V_{dd1}\} \\ 2lmn(-l^2+m^2)V_{dd1} \end{pmatrix}$$

$$r\frac{\partial V_{yz,x^2-y^2}}{\partial \vec{r}} = \begin{pmatrix} lmn[\{2(-l^2+m^2)+1\}V_{dd1}+2V_{dd2}] \\ \frac{1}{2}n[\{(-4m^2+1)(l^2-m^2)-2m^2\}V_{dd1}+2(2m^2-1)V_{dd2}\} \\ \frac{1}{2}m\{(l^2-m^2)(-4n^2+1)V_{dd1}+2(2n^2-1)V_{dd2}\} \end{pmatrix}$$

$$r\frac{\partial V_{zx,x^2-y^2}}{\partial \vec{r}} = \begin{pmatrix} \frac{1}{2}n[\{(-4l^2+1)(l^2-m^2)+2l^2)V_{dd1}+2(-2l^2+1)V_{dd2}\} \\ lmn[\{2(-l^2+m^2)-1\}V_{dd1}-2V_{dd2}] \\ \frac{1}{2}l\{(l^2-m^2)(-4n^2+1)V_{dd1}+2(-2n^2+1)V_{dd2}\} \end{pmatrix}$$

$$r\frac{\partial V_{xy,3z^2-r^2}}{\partial \vec{r}} = \begin{pmatrix} \frac{1}{2\sqrt{3}}m[\{(3n^2-1)(-4l^2+1)-2l^2\}V_{dd1}+4(2l^2-1)V_{dd2}] \\ \frac{1}{2\sqrt{3}}l[\{(3n^2-1)(-4m^2+1)-2m^2\}V_{dd1}+4(2m^2-1)V_{dd2}] \\ \frac{2}{\sqrt{3}}lmn\{(2-3n^2)V_{dd1}+2V_{dd2}\} \end{pmatrix}$$

$$r\frac{\partial V_{yz,3z^2-r^2}}{\partial \vec{r}} = \begin{pmatrix} \frac{1}{\sqrt{3}}lmn\{(1-6n^2)V_{dd1}-2V_{dd2}\} \\ \frac{1}{2\sqrt{3}}n[\{(-4m^2+1)(3n^2-1)-2m^2\}V_{dd1}+2(-2m^2+1)V_{dd2}] \\ \frac{1}{2\sqrt{3}}m[\{(-4n^2+1)(3n^2-1)+4n^2\}V_{dd1}+2(-2n^2+1)V_{dd2}] \end{pmatrix}$$

$$r\frac{\partial V_{zx,3z^2-r^2}}{\partial \vec{r}} = \begin{pmatrix} \frac{1}{2\sqrt{3}}n[\{(-4l^2+1)(3n^2-1)-2l^2\}V_{dd1}+2(-2l^2+1)V_{dd2}] \\ \frac{1}{\sqrt{3}}lmn\{(1-6n^2)V_{dd1}-2V_{dd2}\} \\ \frac{1}{2\sqrt{3}}l[\{(-4n^2+1)(3n^2-1)+4n^2\}V_{dd1}+2(-n^2+1)V_{dd2}] \end{pmatrix}$$

$$r\frac{\partial V_{x^2-y^2,x^2-y^2}}{\partial \vec{r}} = \begin{pmatrix} l\{(l^2-m^2)(-l^2+m^2+1)V_{dd1}+2n^2V_{dd2}\} \\ m\{(l^2-m^2)(-l^2+m^2-1)V_{dd1}+2n^2V_{dd2}\} \\ n\{-(l^2-m^2)^2V_{dd1}+2(n^2-1)V_{dd2}\} \end{pmatrix}$$

$$r\frac{\partial V_{x^2-y^2,3z^2-r^2}}{\partial \vec{r}} = \begin{pmatrix} \frac{1}{\sqrt{3}}l[\{(m^2-l^2)(3n^2-1)+n^2-l^2\}V_{dd1}+2(l^2-m^2-1)V_{dd2}] \\ \frac{1}{\sqrt{3}}m[\{(m^2-l^2)(3n^2-1)-n^2+m^2\}V_{dd1}+2(l^2-m^2+1)V_{dd2}] \\ \frac{1}{\sqrt{3}}n(l^2-m^2)\{(-3n^2+2)V_{dd1}+2V_{dd2}\} \end{pmatrix}$$

$$r\frac{\partial V_{3z^2-r^2,3z^2-r^2}}{\partial \vec{r}} = \begin{pmatrix} ln^2\{(1-3n^2)V_{dd1}-2V_{dd2}\} \\ mn^2\{(1-3n^2)V_{dd1}-2V_{dd2}\} \\ n(1-n^2)\{(3n^2-1)V_{dd1}+2V_{dd2}\} \end{pmatrix}$$

1.2.3 *k*-representation of the Hamiltonian and the overlap matrix

In order to calculate the electronic structure of periodic system, one must use *k*-representation of the Hamiltonian. In the eq. (16),(19)-(22) in p.13 of BICON manual, the *k*-representation of the overlap and the Hamiltonian matrix are explained. [7]

Once the real space expressions of the *S* and *H* matrix is obtained, one must transform

them into k-representation, as shown in BICON manual.

$$S_{st}(\vec{k}) = S_{ss}^{(0,0)} + \sum_{m=1}^{M} \cos(\vec{k} \cdot \vec{R}_m)(S_{st}^{(0,m)} + S_{ts}^{(0,m)}) + i \sum_{m=1}^{M} \sin(\vec{k} \cdot \vec{R}_m)(S_{st}^{(0,m)} - S_{ts}^{(0,m)}),$$
(1.42)

$$S'_{st}(\vec{k}) = S_{ss}^{(0,0)} e^{-\delta(R_{st}^{(0,0)} - d_0)/q_{st}^{(0,0)}}$$
$$+ \sum_{m=1}^{M} \cos(\vec{k} \cdot \vec{R}_m)(S_{st}^{(0,m)} e^{-\delta(R_{st}^{(0,m)} - d_0)/q_{st}^{(0,m)}} + S_{ts}^{(0,m)} e^{-\delta(R_{ts}^{(0,m)} - d_0)/q_{ts}^{(0,m)}})$$
$$+ i \sum_{m=1}^{M} \sin(\vec{k} \cdot \vec{R}_m)(S_{st}^{(0,m)} e^{-\delta(R_{st}^{(0,m)} - d_0)/q_{st}^{(0,m)}} - S_{ts}^{(0,m)} e^{-\delta(R_{ts}^{(0,m)} - d_0)/q_{ts}^{(0,m)}})$$
(1.43)

$$H_{ss}(\vec{k}) = H_{ss}^{(0,0)} S_{ss}(\vec{k}), + 2H_{ss}^{(0,0)} K' \sum_{m=1}^{M} \cos(\vec{k} \cdot \vec{R}_m) S_{ss}^{(0,m)} e^{-\delta(R_{ss}^{(0,m)} - d_0)/q_{ss}^{(0,m)}},$$
(1.44)

$$H_{st}(\vec{k}) = \frac{1}{2}(H_{ss}^{(0,0)} + H_{tt}^{(0,0)})(S_{st}(\vec{k}) + K' S'_{st}(\vec{k})),$$
(1.45)

where the superscripts $(0, m)$ denote the interaction between the origin unit cell and the m-th unit cell.

> In the present code, we can choose either cluster-mode or $\vec{k} = \vec{0}$ periodic mode.

1.2.4   Two-body repulsive energy term

Because all the atomic orbitals are spherical,

$$(E_{\text{Rep}})_{ab} = \frac{Z_a Z_b}{R_{ab}} - \frac{Z_a}{2}\left(\int_0^{R_{ab}} \frac{\rho_b(r)r^2 \mathrm{d}r}{R_{ab}} + \int_{R_{ab}}^{\infty} \frac{\rho_b(r)r^2 \mathrm{d}r}{r}\right) - (\text{counter part } a \leftrightarrow b)$$
(1.46)

from eq. (1.11) and the multipole expansion. [8, 7].

Then, because

$$\rho_b(r) = \sum_{nl} \frac{b_{bnl}^0}{R_{ab}} \frac{(2\zeta_{bnl})^{2n+1}}{(2n)!} r^{2n-2} \exp(-2\zeta_{bnl}r),$$
(1.47)

we obtain

$$
\begin{aligned}
\int_0^{R_{ab}} \frac{\rho_b(r)r^2 \mathrm{d}r}{R_{ab}} &= \sum_{nl} b_{bnl}^0 \frac{(2\zeta_{bnl})^{2n+1}}{(2n)!} \frac{1}{R_{ab}} \int_0^{R_{ab}} r^{2n} \mathrm{e}^{-2\zeta_{bnl}r} \mathrm{d}r \\
&= \sum_{nl} b_{bnl}^0 \frac{(2\zeta_{bnl})^{2n+1}}{(2n)!} \frac{I(2n, 2\zeta_{bnl}, 0) - I(2n, 2\zeta_{bnl}, R_{ab})}{R_{ab}}
\end{aligned}
\tag{1.48}
$$

$$
\begin{aligned}
\int_{R_{ab}}^{\infty} \frac{\rho_b(r)r^2 \mathrm{d}r}{r} &= \sum_{nl} b_{bnl}^0 \frac{(2\zeta_{bnl})^{2n+1}}{(2n)!} \int_{R_{ab}}^{\infty} r^{2n-1} \mathrm{e}^{-2\zeta_{bnl}r} \mathrm{d}r \\
&= \sum_{nl} b_{bnl}^0 \frac{(2\zeta_{bnl})^{2n+1}}{(2n)!} I(2n-1, 2\zeta_{bnl}, R_{ab}),
\end{aligned}
\tag{1.49}
$$

where b_{bnl}^0 denotes an occupation number of nl-orbital in the free (neutral) atom whose species is the same as B atom, and the integral I is defined as eq. (1.29). Then we obtain

$$
\begin{aligned}
&\int_0^{R_{ab}} \frac{\rho_b(r)r^2 \mathrm{d}r}{R_{ab}} + \int_{R_{ab}}^{\infty} \frac{\rho_b(r)r^2 \mathrm{d}r}{r} \\
&= \sum_{nl} b_{bnl}^0 \left[\frac{1}{R_{ab}} - \frac{\mathrm{e}^{-2\zeta_{bnl}R_{ab}}}{2nR_{ab}} \left(2n \sum_{k=0}^{2n} \frac{(2\zeta_{bnl}R_{ab})^k}{k!} - \sum_{k=0}^{2n-1} \frac{(2\zeta_{bnl}R_{ab})^{k+1}}{k!} \right) \right] \\
&= \sum_{nl} b_{bnl}^0 \left[\frac{1}{R_{ab}} - \frac{\mathrm{e}^{-2\zeta_{bnl}R_{ab}}}{2nR_{ab}} \sum_{k=0}^{2n-1} \frac{2n-k}{k!} (2\zeta_{bnl}R_{ab})^k \right].
\end{aligned}
\tag{1.50}
$$

This is the expression in the BICON manual [7] p.14.

The derivative of the E_{Rep} with respect to the variable R_{ab} is required to calculate a term of force originated from the repulsive energy. It is easily obtained from the eqs. (1.46) and (1.29).

$$
\frac{\partial}{\partial R_{ab}} (E_{\mathrm{Rep}})_{ab} = -\frac{Z_a Z_b}{R_{ab}^2} + \frac{Z_a}{2} \int_0^{R_{ab}} \frac{\rho_b(r)r^2 \mathrm{d}r}{R_{ab}^2} + (\text{counter part } a \leftrightarrow b)
\tag{1.51}
$$

Then from eq. (1.48), we obtain

$$
\begin{aligned}
\frac{\partial}{\partial R_{ab}} (E_{\mathrm{Rep}})_{ab} &= -\frac{Z_a Z_b}{R_{ab}^2} + \frac{Z_a}{2} \sum_{nl} b_{bnl}^0 \frac{(2\zeta_{bnl})^{2n+1}}{(2n)!} \frac{I(2n, 2\zeta_{bnl}, 0) - I(2n, 2\zeta_{bnl}, R_{ab})}{R_{ab}^2} \\
&\quad + (\text{counter part } a \leftrightarrow b) \\
&= -\frac{1}{R_{ab}^2} \left(Z_a Z_b - \frac{Z_a}{2} \sum_{nl} b_{bnl}^0 - \frac{Z_b}{2} \sum_{nl} b_{anl}^0 \right) \\
&\quad - \frac{Z_a}{2R_{ab}^2} \sum_{nl} b_{bnl}^0 \mathrm{e}^{-2\zeta_{bnl}R_{ab}} \sum_{k=0}^{2n} \frac{(2\zeta_{bnl}R_{ab})^k}{k!} - (\text{counter part } a \leftrightarrow b)
\end{aligned}
\tag{1.52}
$$

In a periodic system, $E_{\text{Rep}} = \frac{1}{2} \sum_m^M \sum_{a,b} (E_{\text{Rep}}^{(0,m)})_{ab}$, where M is a number of supercell and the superscripts $(0, m)$ denote the interaction between the origin unit cell and the m-th unit cell.

1.3 Special treatments for transition metals $(+\alpha)$

1.3.1 Double-ζ type orbital (for d-orbitals)

In the GENO calculation, the d-orbitals are treated differently from the s- and p-orbitals. Usually, the STO has single screening parameter ζ, as in eq. (1.2). The double-ζ type orbital is defined as the linear combination of two STO's, whose screening parameters are different from each other. Therefore,

$$R_{n2}(r) = \frac{r^{n-1}}{f} \left[c_1 \sqrt{\frac{(2\zeta_1)^{2n+1}}{(2n)!}} \exp(-\zeta_1 r) + c_2 \sqrt{\frac{(2\zeta_2)^{2n+1}}{(2n)!}} \exp(-\zeta_2 r) \right], \tag{1.53}$$

$$f^2 = c_1^2 + c_2^2 + 2c_1 c_2 \left(\frac{4\zeta_1 \zeta_2}{(\zeta_1 + \zeta_2)^2} \right)^{n+\frac{1}{2}}. \tag{1.54}$$

Here, the coefficient c_1 and c_2 are the constants.

1.3.2 Overlap matrix

Because the radial wavefunction of the d-orbitals are double-ζ type orbital instead of single-ζ (STO), the explicit expression of the overlap relevant to d-obitals is changed.

Between s-, p-orbitals and d-orbital

We assume, in this sub-subsection, that $\vec{r}_a = \vec{r}_b + R_{ab}(0,0,1)^T$ and the wavefunction of the d-orbitals on the B atom are expressed by double-ζ orbitals,

$$\phi_{n_b 2 m_b}(\vec{r} - \vec{r}_b) = \frac{c_1}{f} \phi_{n_b 2 m_b}^{(\text{STO},\zeta_1)}(\vec{r} - \vec{r}_b) + \frac{c_2}{f} \phi_{n_b 2 m_b}^{(\text{STO},\zeta_2)}(\vec{r} - \vec{r}_b), \tag{1.55}$$

where $\phi_{nlm}^{(\text{STO},\zeta)}(\vec{r}) = \sqrt{\frac{(2\zeta)^{2n+1}}{(2n)!}} \exp(-\zeta r) Y_{lm}(\theta, \varphi)$. Then the overlap is expressed as

$$\left\langle \phi_{n_b 2 m_b} \middle| \phi_{n_a l_a m_a}^{(\text{STO},\zeta_a)} \right\rangle = \frac{c_1}{f} \left\langle \phi_{n_b l_b m_b}^{(\text{STO},\zeta_1)} \middle| \phi_{n_a l_a m_a}^{(\text{STO},\zeta_a)} \right\rangle + \frac{c_2}{f} \left\langle \phi_{n_b l_b m_b}^{(\text{STO},\zeta_2)} \middle| \phi_{n_a l_a m_a}^{(\text{STO},\zeta_a)} \right\rangle. \tag{1.56}$$

Here, the each term in the right hand side is expressed by the eq. (1.26).

This expression corresponds to the case of the direction cosines $(l, m, n) = (0, 0, 1)$, and gives the expressions for $V_{sd\sigma}$, $V_{pd\sigma}$ and $V_{pd\pi}$ in the sec. 1.2.2. Other (l, m, n) cases are obtained from the Slater-Koster table (See s-d or p-d case).

Between two d-orbitals

Similar to the case in the previous sub-subsection. We assume that

$$\phi_{n_a 2 m_a}(\vec{r} - \vec{r}_a) = \frac{c_1}{f_a} \phi_{n_a 2 m_a}^{(\text{STO},\zeta_1)}(\vec{r} - \vec{r}_a) + \frac{c_2}{f_a} \phi_{n_a 2 m_a}^{(\text{STO},\zeta_2)}(\vec{r} - \vec{r}_a),$$

$$\phi_{n_b 2 m_b}(\vec{r} - \vec{r}_b) = \frac{c_3}{f_b} \phi_{n_b 2 m_b}^{(\text{STO},\zeta_3)}(\vec{r} - \vec{r}_b) + \frac{c_4}{f_b} \phi_{n_b 2 m_b}^{(\text{STO},\zeta_4)}(\vec{r} - \vec{r}_b). \tag{1.57}$$

Then the overlap between them is expressed as the following bilinear-form of (c_1, c_2) and (c_3, c_4);

$$\left\langle \phi_{n_b 2 m_b} \middle| \phi_{n_a 2 m_a} \right\rangle = \frac{c_3 c_1}{f_a f_b} \left\langle \phi_{n_b l_b m_b}^{(\text{STO},\zeta_3)} \middle| \phi_{n_a l_a m_a}^{(\text{STO},\zeta_1)} \right\rangle + \frac{c_4 c_1}{f_a f_b} \left\langle \phi_{n_b l_b m_b}^{(\text{STO},\zeta_4)} \middle| \phi_{n_a l_a m_a}^{(\text{STO},\zeta_1)} \right\rangle$$

$$+ \frac{c_3 c_2}{f_a f_b} \left\langle \phi_{n_b l_b m_b}^{(\text{STO},\zeta_3)} \middle| \phi_{n_a l_a m_a}^{(\text{STO},\zeta_2)} \right\rangle + \frac{c_4 c_2}{f_a f_b} \left\langle \phi_{n_b l_b m_b}^{(\text{STO},\zeta_4)} \middle| \phi_{n_a l_a m_a}^{(\text{STO},\zeta_2)} \right\rangle. \tag{1.58}$$

The above expression corresponds to the case $(l, m, n) = (0, 0, 1)$ and gives the expressions for $V_{dd\sigma}$, $V_{dd\pi}$ and $V_{dd\delta}$ in the sec. 1.2.2. For the other cases, the expression of the overlaps are obtained from Slater-Koster table of the d-d case.

1.3.3 Diagonal part of the Hamiltonian

The diagonal part of the Hamiltonian (valence state ionization energy, VSIE or valence orbital ionization potential, VOIP) for the transition metal is different from that of the atoms whose valence electrons consist of s- or/and p-electrons. Here we define the σ, π, δ so as to express the fractional occupation number of the respective orbitals on transition-metal atoms,

$$\sigma = \sum_{\substack{\alpha:s\text{-orbit},j,\beta, \\ k:\text{ occupied}}} c_{i\alpha}^k c_{j\beta}^k S_{i\alpha,j\beta}, \tag{1.59}$$

$$\pi = \sum_{\substack{\alpha:p\text{-orbit},j,\beta, \\ k:\text{ occupied}}} c_{i\alpha}^k c_{j\beta}^k S_{i\alpha,j\beta}, \tag{1.60}$$

$$\delta = \sum_{\substack{\alpha:d\text{-orbit},j,\beta, \\ k:\text{ occupied}}} c_{i\alpha}^k c_{j\beta}^k S_{i\alpha,j\beta}, \tag{1.61}$$

then the $VOIP(d^\delta s^\sigma p^\pi)$ is expressed as

$$VOIP_s(d^\delta s^\sigma p^\pi)$$
$$= (2 - \sigma - \pi) VOIP_s(d^{n-1} s^1) + (\sigma - 1) VOIP_s(d^{n-2} s^2) + \pi VOIP_s(d^{n-2} s^1 p^1) \tag{1.62}$$

$$VOIP_p(d^\delta s^\sigma p^\pi)$$
$$= (2 - \sigma - \pi) VOIP_p(d^{n-1} p^1) + (\pi - 1) VOIP_p(d^{n-2} p^2) + \sigma VOIP_p(d^{n-2} s^1 p^1) \tag{1.63}$$

$$VOIP_d(d^\delta s^\sigma p^\pi)$$
$$= (1 - \sigma - \pi) VOIP_d(d^n) + \sigma VOIP_d(d^{n-1} s^1) + \pi VOIP_d(d^{n-1} p^1) \tag{1.64}$$

where $Q = Z - \sigma - \pi - \delta$ and $n = $ (# of electrons in the reference system), possibly $n = Z$.[5] One should take care for the confusion between the number of electron and the principle quantum number. Here in this subsection, n denotes the the number of the electrons.

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[5]In the section 5.3.2 of the ICON manual, $VOIP_p(d^\delta s^\sigma p^\pi)$ has different expression. But the present author believes that the expression in the ICON manual (eq.(5.185)) is typography. There are two reasons for his belief. (i) If the occupation number of the p-orbital is equal to zero, one can not define the ionization potential for p-orbital. (ii) The average occupation number of p-orbital is not equal to π, if one assume the eq.(5.185) in the ICON manual is correct.

Chapter 2

Attaching the ICON calculation to ELSES package

Because GENO calculation uses overlap matrix, as is in the NRL type calculation, the data flow of the GENO calculation is quite similar to that of NRL type calculation. In the present NRL type calculation codes, the density matrix and the energy density matrix are calculated in the topmost layer of the ELSES package, as is shown in the figure (2.1).

Now the data flow and the calling sequence of the GENO module in the ELSES package is explained in the figure (2.2), schematically, with a structure of a charge consistency loop of GENO calculation.

2.1 Outlook of this module

In the GENO calculation, first, one must read the some related constants, numbers of valence electrons on s-, p- and d- orbitals, principal quantum numbers of respective orbitals, screening parameter ζ of each STO's, e.t.c ... . These constants are listed in the
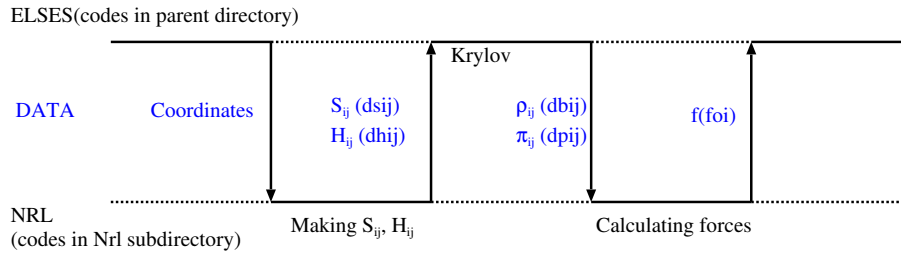
Figure 2.1: Schematic data flow of NRL type calculation. The Hamiltonian and the overlap matrices are denoted as H_{ij} and S_{ij}. The density and the energy density matrices are denoted as ρ_{ij} and π_{ij}. The force vector is denoted as f. The name of the arrays where the respective data are stored is written in the parentheses.
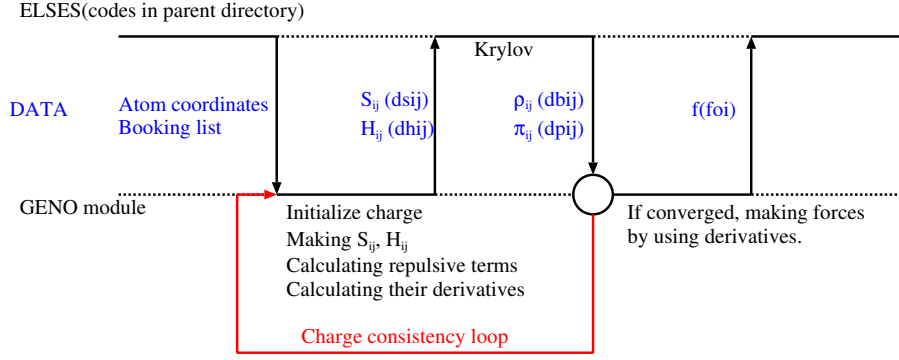
Figure 2.2: Schematic data flow of GENO calculation. The symbols are shared with the figure (2.1). In comparison with NRL calculation, charge consistency loop is added to the structure.

table 2.1. Second, the overlap matrix S_{st} are calculated with the expressions eq. (1.26), (1.37) and (1.38). Then, the diagonal element of Hamiltonian is calculated as

$$H_{ii}(\text{or } H_{ss} \text{ in the BICON expression}) = -VOIP(Q) = -(d_0 + d_1 Q + d_2 Q^2) \qquad (2.1)$$

Next, the non-diagonal element H_{ij} is calculated as

$$\Delta = \frac{H_{ii} - H_{jj}}{H_{ii} + H_{jj}}, \qquad (2.2)$$

$$r_0 = \frac{n_a}{\zeta_a} + \frac{n_b}{\zeta_b}, \qquad (2.3)$$

$$q = 1 + \{[(R - r_0) - |R - r_0|]\delta\}^2, \qquad (2.4)$$

$$K' = \kappa + \Delta^2 - \Delta^4 \kappa \qquad (2.5)$$

$$K = 1 + K' \exp[-\delta(R - r_0)/q] \qquad (2.6)$$

$$H_{ij} = K \frac{H_{ii} + H_{jj}}{2} S_{ij}, \qquad (2.7)$$

where i-orbital is on A atom (with the suffix "a").

The Hamiltonian and the overlap matrix are treated in the upper layer of ELSES code, then the module receive the density matrix and the energy density matrix. The Mulliken charge is calculated by using the density matrix and the overlap matrix, as in the eq. (1.3). The summation of the single-electron state energy is obtained as a trace of the energy density matrix.

One must calculate the two-body repulsive (in the neutral atom case) term shown in the eq. (1.50). And finally, one must calculate the force by using the derivatives.

Table 2.1: Periodic table of elements. The boxed cell shows the elements whose parameters for the calculation we can borrow from the ICON package.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	[H]																	He
2	[Li]	[Be]											[B]	[C]	[N]	[O]	[F]	Ne
3	[Na]	[Mg]											[Al]	[Si]	[P]	[S]	[Cl]	Ar
4	K	Ca	Sc	Ti	[V]	[Cr]	[Mn]	[Fe]	[Co]	[Ni]	[Cu]	[Zn]	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	[Mo]	Tc	[Ru]	[Rh]	Pd	[Ag]	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Ac															

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw

2.2 Module variables

Mulliken charge (per orbital), STO and double-ζ type orbital parameters, VOIP parameters, κ, δ in the eq. (1.6) and (1.7), the Hamiltonian and the overlap matrices.

2.3 Subroutines

2.3.1 Subroutine initializes the module variable

Element-specific parameters are stored in the module variable "AtomParameter". This subroutine initializes "AtomParameter"

2.3.2 Function A and B

- Input: n and λ

- Output: Returns the value of A and B, respectively Set the derivative w.r.t R to an argument.

See the equations (1.37), (1.39), (1.38) and (1.40).

2.3.3 Subroutine calculates submatrix of overlap matrix

- Input: Integer specifire of the elements of the bra and ket STO's, relative coordinate.

- Output: The submatrix of the overlap matrix. The derivative of the overlap matrix w.r.t R_{ab}.

Table 2.2: STO parameters for main atoms in the ICON module. Imported from the file "ATOMDEF.DAT" in the program package distributed on the ICON web site. [2] The parameter U gives the atomic energy level. Initially, the levels are occupied in the order of U values.

| spec | Z | (ns) | | | (np) | | | (nd) | | |
		n	ζ	U	n	ζ	U	n	ζ	U
H	1	1	1.3	-13.6						
He	2	1	1.688	-23.4						
Li	1	2	0.65	-5.4	2	0.65	-3.5			
Li^M	1	2	0.703	-9.0	2	0.703	-8.0			
Be	2	2	0.975	-10.0	2	0.975	-6.0			
B	3	2	1.300	-15.2	2	1.300	-8.5			
C	4	2	1.710	-21.4	2	1.625	-11.4			
N	5	2	2.140	-26.0	2	1.950	-13.4			
O	6	2	2.575	-28.2	2	2.275	-12.4			
F	7	2	3.010	-40.0	2	2.425	-18.1			
F$^-$	7	2	2.425	-34.8	2	2.225	-14.4			
Na	1	3	0.733	-5.1	3	0.733	-3.0			
Na^M	1	3	0.815	-8.5	3	0.815	-6.25			
Mg	2	3	1.100	-9.0	3	1.100	-4.5			
Al^M	3	3	1.167	-12.3	3	1.167	-6.5			
Al^{+3}	3	3	1.500	-16.31	3	1.500	-10.00			
Si	4	3	1.383	-17.3	3	1.383	-9.2	0?	0.667?	-6.0?
Si^{+2}	4	3	1.600	-20.44	3	1.600	-12.41	0?	0.667?	-6.0?
Si^{+3}	4	3	1.700	-21.68	3	1.700	-13.39	0?	0.667?	-6.0?
P	5	3	1.600	-18.6	3	1.300	-14.0			
S	6	3	2.283	-20.5	3	1.817	-11.4	0?	1.500?	-8.0?
Cl	7	3	2.183	-36.3	3	1.733	-14.2	0?	1.167?	-9.0?

? : Possibly not available (marked orbitals may not be included in the calculation).
^{M} : Parameter for the atom in the metallic system.

Table 2.3: VOIP parameters for main atoms in the ICON module. Imported from the file "VOI.DAT" in the program package distributed on the ICON web site. [2]

spec	$d2_s$	$d1_s$	$d0_s$	$d2_p$	$d1_p$	$d0_p$
H	13.618	27.18	13.6	0.0000	0.000000	0.000000
Li	3.4244	9.42287	5.38095	3.43934	7.32752	3.52117
Be	3.426951	12.4357138	9.3112879	3.441829	10.079996	5.938891
B	3.449268	14.952614	14.0599203	3.444308	12.6960831	8.2760115
C	3.465386	17.556303	19.4160805	3.465386	14.655049	10.6379290
N	3.491423	20.110397	25.5657463	3.491423	16.514828	13.1920233
O	3.465386	22.887665	32.3353348	3.464146	18.566782	15.7957125
F	3.480264	25.503753	40.1216049	3.462906	20.519548	18.6473713
Ne	3.507541	28.144638	48.4658127	3.502582	22.342131	21.5610237
Na	1.6341248	8.4309931	5.0833931	1.6527227	6.1248687	2.9632462
Mg	1.6279255	9.6956415	7.5940928	1.6291650	9.7452360	8.8893860
Al	1.642804	11.034682	11.2578545	1.6477633	8.8153467	5.9326911
Si	1.621726	12.38612	14.8286285	1.614287	10.1295900	7.7490745
P	1.769269	13.229219	18.7713566	1.890774	10.402357	10.1171913
S	1.516339	15.374164	20.6683311	1.632885	12.212542	11.5802164
Cl	1.698597	15.708923	25.2681808	1.67256	13.179626	13.6879644
Ar	1.641564	17.184347	29.2109108	1.656442	14.456674	15.8081121
K	1.0030401	6.6332078	4.3022857	1.3434000	4.4932000	2.7290000

Table 2.4: STO parameters for transition metals+α in the ICON module. Imported from the file "ATOMDEF.DAT" in the program package distributed on the ICON web site. [2]

spec	Z	n	ζ (ns)	U	n	ζ (np)	U	n	ζ_1 (nd)	U	c_1	ζ_2	c_2
Sc	3	4	1.300	-8.87	4	1.300	-2.75	3	4.340	-8.51	.423	1.700	.727
Ti	4	4	1.075	-8.97	4	0.675	-5.44	3	4.550	-10.81	.421	1.400	.784
Ti^M	4	4	1.500	-6.30	4	1.500	-3.20	3	4.550	-5.9	.421	1.400	.784
Ti$^+$	4	4	1.311	-13.00	4	1.088	-8.92	3	4.231	-16.89	.468	1.673	.686
V	5	4	1.300	-8.81	4	1.300	-5.52	3	4.750	-11.00	.475	1.700	.705
V^M	5	4	1.600	-6.70	4	1.600	-3.40	3	4.750	-6.70	.475	1.500	.752
V$^+$	5	4	1.376	-13.00	4	1.134	-8.92	3	4.617	-16.89	.472	1.858	.678
Cr	6	4	1.700	-8.66	4	1.700	-5.24	3	4.950	-11.22	.506	1.800	.675
Cr^{+3}	6	4	1.525	-13.01	4	1.025	-8.949	3	4.950	-16.89	.525	2.200	.629
Cr^M	6	4	1.700	-7.30	4	1.700	-3.60	3	4.950	-7.90	.487	1.600	.720
Mn	7	4	1.800	-9.75	4	1.800	-5.89	3	5.150	-11.67	.532	1.900	.693
Mn^{+2}	7	4	1.650	-10.03	4	1.150	-6.06	3	5.150	-12.43	.547	2.100	.605
Mn^M	7	4	1.800	-7.50	4	1.800	-3.80	3	5.150	-8.70	.514	1.700	.693
Fe	8	4	1.900	-9.10	4	1.900	-5.32	3	5.350	-12.60	.550	2.000	.626
Fe^M	8	4	1.900	-7.60	4	1.900	-3.80	3	5.350	-9.20	.537	1.800	.668
Fe^{+2}	8	4	1.575	-9.645	4	0.975	-5.90	3	5.350	-12.00	.565	2.300	.585
Fe^{+3}	8	4	1.575	-10.165	4	0.975	-6.14	3	5.350	-12.50	.583	2.300	.542
Co	9	4	2.000	-9.21	4	2.000	-5.29	3	5.550	-13.18	.568	2.100	.606
Co^M	9	4	2.000	-7.80	4	2.000	-3.80	3	5.550	-9.70	.555	1.900	.668
Ni	10	4	1.825	-9.17	4	1.125	-5.15	3	5.750	-13.49	.568	2.000	.630
Ni^M	10	4	2.100	-7.80	4	2.100	-3.70	3	5.750	-9.90	.568	2.000	.629
Cu	11	4	2.200	-11.40	4	2.200	-6.06	3	5.950	-14.00	.593	2.300	.574
Cu$^+$	11	4	2.200	-12.00	4	2.200	-7.50	3	6.684	-15.600	.486	2.777	.657
Zn	12	4	1.633	-8.00	4	1.042	-4.40	3	7.015	-21.30	.487	2.911	.656
Zn$^+$	12	4	1.770	-8.00	4	1.396	-4.40	3	7.024	-21.30	.486	2.921	.656
Rb	1	5	0.994	-0.00	5	0.694	-0.00	3	0.000?	-00.00?			
Y	3	5	1.390	-8.60	5	1.390	-5.00	4	4.330	-8.40	.5827	1.400	.677
Mo	6	5	1.480	-10.40	5	1.072	-6.87	4	3.126	-14.90	.717	1.408	.426
Ru	8	5	1.575	-10.40	5	1.134	-6.87	4	3.429	-14.90	.780	1.453	.368
Ru^{+2}	8	5	2.08	-9.23	5	2.04	-5.78	4	5.38	-14.14	.534	2.300	.637
Rh	9	5	1.617	-12.00	5	1.160	-7.50	4	3.577	-15.60	.805	1.452	.348
Ag	11	5	1.697	-7.57	5	1.201	-3.80	4	3.912	-12.70	.825	1.545	.329
Ag$^+$	11	5	1.842	-9.24	5	1.492	-7.12	4	3.921	-13.68	.823	1.565	.328
In	0	5	1.903	-12.60	5	1.677	-6.19	0	0.0?	0.0?			
Re	7	6	1.845	-6.38	6	1.250	-3.98	5	3.734	-12.35	.732	1.742	.424
Os	8	6	1.891	-6.55	6	1.280	-4.00	5	3.857	-13.74	.760	1.797	.390
Pt	10	6	1.972	-9.08	6	1.333	-5.48	5	4.084	-12.59	.798	1.840	.352
Pt$^+$	10	6	2.095	-9.08	6	1.703	-5.48	5	4.094	-12.59	.797	1.862	.349
Au	11	6	2.602	-10.92	6	2.584	-5.55	4	6.163	-15.07	.644	2.794	.536

Table 2.5: VOIP parameters for main atoms in the ICON module. Imported from the file "FOI.DAT" in the program package distributed on the ICON web site. [2] There are nine parameters per each atom specie per azimuthal angular momentum s, p and d. (See the section 1.3.3.)

spec	$d2_{\mathrm{conf}}$	$d1_{\mathrm{conf}}$	$d0_{\mathrm{conf}}$	$d2_{\mathrm{conf}}$	$d1_{\mathrm{conf}}$	$d0_{\mathrm{conf}}$
Zr	0.6261252	5.982285	6.224057	0.8678963	6.385237	6.943171
	1.004280	5.418153	8.257414	0.6695201	4.947010	3.694759
	0.9794830	4.525459	4.513061	0.9794830	4.525459	5.083393
	0.8183023	7.662285	3.855940	0.8245015	8.201621	5.678522
	0.8864942	8.015643	6.769591			
Ag	0.5500000	8.390000	7.580000	0.3700000	8.880000	8.800000
	0.3100000	9.710000	10.230000	0.7700000	6.460000	3.830000
	1.1800000	6.860000	8.120000	1.1800000	6.860000	4.760000
	3.9000000	25.600000	0.000000	0.4600000	12.660000	12.770000
	0.8100000	11.670000	14.490000			
Nb	0.5517341	6.391437	6.546418	0.5083393	7.203539	7.439112
	0.9732838	5.573134	8.840144	0.5393355	5.387156	3.843541
	0.7129149	4.965607	4.736235	0.7129149	5.089592	5.517341
	0.6695201	8.579775	4.525459	0.7005163	8.970328	6.472027
	0.8926933	8.505384	7.897857			
Mo	0.4959408	6.781990	6.819186	0.1239852	8.220219	7.637488
	0.8616971	5.895496	9.336085	0.4463467	5.777710	3.942729
	0.4959408	5.356161	4.959408	0.4959408	5.356161	5.951289
	0.5703319	9.360882	5.244574	0.6013282	9.689443	7.761473
	0.8802949	9.063317	8.976528			
Tc	0.4401474	7.197340	7.042359	-8.6789630E-02	8.840144	7.935052
	0.7005163	6.366640	9.732838	0.3905534	6.118669	3.992323
	0.5021400	5.697120	5.009002	0.5021400	5.697120	6.385237
	0.5145386	10.02420	6.013282	0.5269371	10.37136	8.778152
	0.8740956	9.577856	10.10479			
Ru	0.4091511	7.587894	7.215938	-0.1983763	9.286491	8.183022
	0.4959408	6.967968	10.04280	0.3781548	6.391437	4.004722
	0.5889297	5.969887	5.046197	0.5889297	5.969887	6.819186
	0.5331364	10.51394	6.831584	0.4711437	11.02228	9.782432
	0.8554978	10.12959	11.18346			
Rh	0.4029519	7.953650	7.352322	-0.1983763	9.522063	8.406197
	0.2603689	7.662285	10.29077	0.4091511	6.608411	3.955127
	0.8926933	6.062876	5.046197	0.8926933	6.062876	7.253134
	0.6261252	10.83011	7.699480	0.4215497	11.67941	10.74952
	0.8307008	10.72472	12.24974			
Pd	0.4029519	8.325605	7.439112	-9.9188156E-02	9.584056	8.579775
	-6.1992597E-02	8.616971	10.36516	0.4649445	6.800588	3.855940
	1.035276	6.379038	4.984205	1.035276	6.379038	7.687082
	0.7749075	11.01608	8.616971	0.4339482	12.20014	11.74140
	0.4339482	12.42332	12.57210			

Table 2.6: (Continued from the Table 2.5) VOIP parameters for main atoms in the ICON module. Imported from the file "FOI.DAT" in the program package distributed on the ICON web site. [2]

spec						
Cr	.9980500	7.13513	6.59581	.9980500	8.28815	7.84802
	.9980500	7.49467	9.26140	.8988600	5.89530	3.52100
	.8988600	6.55240	4.68650	.8988600	6.55240	4.72369
	1.8287000	9.26760	4.35170	1.2088000	11.89600	7.17850
	1.2088000	12.01990	8.39350			
Mn	.9420000	7.55000	6.85600	.9420000	8.71600	8.17000
	.9420000	7.91000	9.70800	.8930000	6.11000	3.62000
	.8930000	6.84000	4.81000	.8930000	6.84000	4.88000
	1.7480000	10.01800	4.78600	.6820000	13.01800	7.94700
	.6820000	13.01800	9.21200			
Fe	.9110000	7.91600	7.10400	.911	9.057	8.468
	.911	8.35	10.092	.905	6.298	3.707
	.905	7.166	4.922	.905	7.166	4.996
	1.711	10.687	5.195	1.711	12.584	8.678
	1.711	12.634	10.067			
Co	.8989	8.263	7.327	.8989	9.3296	8.7407
	.8989	8.846	10.4144	.93603	6.4408	3.806
	.93603	7.5195	5.046	.93606	7.5195	5.058
	1.71714	11.3009	5.554	1.71714	13.173	9.373
	1.71714	13.0862	10.96			
Ni	.911	8.56	7.538	.911	9.55	8.963
	.911	9.379	10.662	.9856	6.552	3.893
	.9856	7.903	5.133	.9856	7.903	5.07
	1.76	11.84	5.9	1.76	13.724	10.03
	1.76	13.414	11.889			
Cu	.942	9.459	7.724	.942	9.683	9.174
	.942	9.955	10.86	.434	7.253	3.98
	.434	9.993	5.281	.434	9.993	5.033
	1.773	16.117	2.48	1.773	14.307	10.662
	1.773	13.699	12.856			
Zn	1.004	9.026	7.935	1.004	9.732	9.335
	1.004	18.039	10.984	1.066	6.844	3.967
	1.066	7.538	5.393	1.066	7.463	4.947
	0.0	11.902	16.043	0.0	11.902	16.043
	0.0	10.972	18.597			
V	1.06	6.71359	6.32305	1.06	7.80463	7.48847
	1.06	7.13513	8.75308	.92366	5.63495	3.43428
	.92366	6.30445	4.56251	.92366	6.30445	4.51292
	1.9589	8.43073	3.89301	1.7357	10.7864	6.37264
	1.7357	10.8236	7.61			

See the eq. (1.26), (1.56), and (1.58).

This subroutine calls A and B function in the section 2.3.2.

At the end of this subroutine, rotate the coordinate system by using Slater-Koster table.

2.3.4 Subroutine calculates diagonal submatrix of Hamiltonian

- Input: Integer specifire of the elements.

- Output: The diagonal submatrix of the Hamiltonian.

See the eq's (1.4), (1.62), (1.63) and (1.64).

2.3.5 Subroutine calculates non-diagonal submatrix of Hamiltonian

- Input: Integer specifire of the elements, relative coordinates, diagonal submatrix of the Hamiltonian.

- Output: The non-diagonal submatrix of the Hamiltonian.

See the eq's (1.5), (1.6), (1.7), (1.8), (1.9).

2.3.6 Calculation of two-body repulsive part

- Input: Integer specifire of the elements, relative coordinates.

- Input: Occupation and zeta (module variable).

- Output: The two body repulsive part and the array of its derivatives w.r.t. R_{ab}'s.

2.3.7 Calculating total energy

See the eq's (1.10) and (1.11)

2.3.8 Making forces

See the section 1.2.2.

Bibliography

[1] G. C. Calzaferri, L. Forss, and I. Kamber, J. Phys. Chem., **93** 5366 (1989).

[2] Prof. Calzaferri's home page on http://iacrs1.unibe.ch/start.html .

[3] *"Extended Hückel Molecular Orbitals and Oscillator Strength Calculations, ICON-EDiT Manual"*, Gion Calzaferri, Stephan Glaus, Dominik Brühwiler, on
http://iacrs1.unibe.ch/program/iconedit.html
(1997).

[4] M. Wolfsberg and L. Helmholz, J. Chem. Phys., **20**, 837 (1952).

[5] Gion Calzaferri and Ruedi Rytz, J. Phys. Chem. **100**, 11122 (1996).

[6] J. H. Ammeter, H.-B. Bürgi, J. C. Thibeault, and R. Hoffmann, J. Am. Chem. Soc., **100**, 3686 (1978).

[7] *BICON-CEDiT, Extended Hückel Band Structure and Crystal Electronic Dipole induced Transitions Calculations Manual* , Martin Brändle, Ruedi Rytz and Gion Calzaferri, on
http://iacrs1.unibe.ch/program/biconcedit.html
http://iacrs1.unibe.ch/download/BICONCEDIT/manual.pdf
(1997).

[8] G. Calzaferri, L. Forss, and I. Kamber, J. Phys. Chem. **93**, 5366 (1989).

[9] http://en.wikipedia.org/wiki/Prolate_spheroidal_coordinates. We cited the public domain figure 1.2 from wiki.