Comparison of Finite Element Approach and LCAO Analysis with SIWB Method for a Molecule Including an Anion in a Discrete Variational Density Functional Theory

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An anion (negative ion) such as O^{2-} , which is stable in a molecule/solid, sometimes cannot bind an attached electron in a vacuum and emits an electron. To describe an anion, the author previously developed the SIWB (surrounding or solid Coulomb-potential-induced well for basis set) method for a linear combination of atomic orbitals (LCAO) calculated numerically in a discrete variational (DV) density functional theory (DFT). For the generation of basis atomic orbitals, the DV method usually adds a well potential to the potential for electrons to stabilize the electrons. There was no reasonable method for determining the depth and radius of the well and the usual well depth has a relatively deep value of about -1 Eh independent of electron attachment tendency. In contrast, the SIWB method adds a well potential solely for generating and improving anion basis atomic orbital functions and uniquely determines the depth and radius of the well, which is relatively shallow, considering the Coulomb potential arising from the surrounding nuclei and electron cloud in a molecule/solid. This article aims to attempt calculations for the one-electron wave function of a molecule including an anion using the finite element method, which adopts a basis set localized in a small region on a space lattice that is suitable for the wave function behavior of an anion. The finite element results were compared not only to results from the usual LCAO method with a relatively deep well (denoted as LCAO–N), but also to those from the improved LCAO method with the SIWB scheme (denoted as LCAO–SIWB). It emerged from the present study that the finite element results for the anion are consistent with the LCAO–SIWB results.

Keywords: Finite element theory, LCAO, Well radius/depth for anion basis set, DFT

1 Introduction

The anions (negative ions) addressed in this paper form ionic molecules as well as solids, which sometimes reveals a peculiar feature of the anions such as O^{2-} for preferential stable existence in a solid, despite the electron emission in a vacuum. This property may give rise to the unexpected phenomena encountered by theoretical electronic state calculations, and the author has attributed the antiferromagnetism in copper oxides to this anion property with delocalized electrons [1–4]. The physical and chemical properties of magnetic materials have been widely investigated and applied, such as in memory storage [5]. The

significant progress of density functional theory (DFT) [6–8] has led to a tremendous increase in theoretical investigations on the electronic state of materials using the linear combination of atomic orbitals (LCAO). The discrete variational (DV) method [9,10] employs a basis set of atomic orbitals calculated numerically and adds a well potential as in Figure 1. In the case of oxygen, an isolated O^- is experimentally observed in a vacuum [11–13], but an isolated O^{2-} is not observed in a vacuum. The reason for adding a well potential in the DV method is to stabilize and improve the unstable atomic orbitals of the electrons on an isolated anion. Usually the well depth is chosen as relatively deep, about -1.0 Eh as well as the well radius of about 3.5 a.u.,

Figure 1. Schematic illustration of the well potential.

and as independent of the electron attachment tendency.

In the conventional DV method there was no reasonable method for determining the depth and radius of the well. One of the present authors developed the method referred to as the SIWB (surrounding or solid Coulomb-potential-induced well for basis set), which determines the depth and the radius of the well potential uniquely by taking into account the surrounding Coulomb potential in a molecule/solid [2]. The depth of the well becomes shallower than that of the conventional DV method, which improves the basis set for negative ions suitably.

The well potential within an anion radius, which is to be described in detail in the section 2.1, is related to the summed Coulomb potentials originated from nuclei and electron clouds surrounding an anion placed at the center. For the molecule, the value of the well potential is chosen to be zero at the point far apart from the molecule. For the solid, the spherically averaged value of the well depth is calculated by employing the Evjen method [14–17], and measured relative to the maximum potential averaged over a thin spherically divided domain away from the central anion nucleus.

For the Cu oxides such as CaCuO_2 which is a mother material of superconductors, the SIWB method generates the relatively shallower well than the usual DV well depth (about -1.0 Eh). The conventional DV method leads to the nonmagnetic metal. The LCAO–SIWB method derives delocalized electrons on the oxygen anion sites through the shallower well, and gives rise to the antiferromagnetism with the lower total energy. It is because the total energy of the antiferromagnetic state is lower

than the nonmagnetic metallic state, since the antiparallel magnetic attraction between nearest neighbor spins makes the total energy lower than the energy of the nonmagnetic state. This means that the basis set is improved, since the total energy lowers.

The LCAO wave functions considered previously were the linear superposition of atomic orbitals solved from one-dimensional (1D) numerical differential equations for radial functions. In this paper we emphasize the use of the numerical calculation of one-electron wave functions in an entire system including anions beyond the LCAO treatment. For quantum electrodynamics, the authors developed the finite element method [18,19] where we expand a wave function in terms of local pyramid functions on a lattice and the wave function is linearly interpolated between lattice points [20]. The basic equation of the finite element approach is similar to the difference equation, but is contrastingly superior to the difference equation in tractable flexibility.

Following these papers we apply the finite element method to the present molecular case and we replace the large scale basis atomic orbitals on atoms in the LCAO scheme by the small scale local basis functions on lattice points. It is expected that the finite element method may offer an advantage in that the results obtained will be plausible for a system including anions. This is because the finite element method does not explicitly use the atomic orbitals of an isolated anion, but directly calculates the wave functions in a molecule/solid. The finite element method presently consumes much longer computation time and a large amount of memories than the LCAO method, and it is not yet suitable for large calculations. Consequently, in this paper we specifically explore an extremely small axis-symmetric LiH molecule. The results obtained are elucidated to provide a comparison between the results obtained using the LCAO method with the well depth of about -1 Eh (labeled as LCAO–N) and the results obtained using the improved LCAO method with the SIWB method (labeled as LCAO–SIWB).

The next section presents the theoretical formalism of the finite element method after briefly summarizing the LCAO method including the SIWB method. The section also describes a molecule with focus on the calculation conditions. The subsequent section reports the calculated results and compares them with those obtained using the aforementioned methods. Conclusions follow with confirmation of the results obtained.

2 Theoretical Methods

2.1 LCAO with associated methods in a DFT and SIWB procedure

Toward comparison of the LCAO scheme, including the SIWB (surrounding or solid Coulomb-potential-induced well for basis set) method developed by the present author, with the finite element method presented in the next subsection, this section starts with a brief description of the LCAO formalism and incorporated numerical calculation methods. Basic principles of the density functional theory (DFT) approach are supported by the Hohenberg–Kohn theorem that the ground state is described in terms of the electron density under the Coulomb potential produced from nuclei [6]. The exchange-correlation terms in the density functional form are practical but the final exact form may have not been known. The analysis results in the scheme may be compensated by the approaches from such as Hartree–Fock with perturbation MP2 and CCSD.

The discrete variational (DV) method in the Kohn–Sham formalism uses basis atomic orbitals calculated numerically and the matrix elements are integrated numerically using the Diophantine (weighted Monte Carlo) procedure. The DV method usually uses the SCC (self-consistent charge) approximation in the process of self-consistent iterations. Electron populations on basis atomic orbitals are calculated via the Mulliken population analysis [21]. Electron densities are derived from radial functions of atomic orbitals multiplied by the electron population, resulting in that the electron charge density on an atom becomes spherically symmetric. The Coulomb potential induced from spherical charges of an atom/ion is simplified to a one-dimensional integral in spherical coordinates. The total electron density of the total multi-atomic system in the SCC approximation is the superposition of electron densities on constituent atoms. Total electronic Coulomb potential is also the superposition of electronic Coulomb potentials on constituent atoms.

Radial functions of numerical basis atomic orbitals $R_j(r)$ with kinetic and potential terms $T_A(r)$ and $U_A(r)$, respectively, and eigen values ε_j are derived by solving a quantum wave equation

$$[T_A(r) + U_A(r)]R_j(r) = \varepsilon_j R_j(r) \quad (1)$$

for an isolated atom/ion.

The SIWB method, which the present author developed, determines the depth of the well potential within a well radius for generating the numerical basis set as follows. In the molecule case, the spherically symmetric domain around a central nega-

tive ion nucleus is divided into subdomains. (The outer and inner radii of each subdomain are to be denoted below.) The well region within a well radius has from one to several subdomains. The well potential is constructed using the Coulomb potential V at $\mathbf{r}$ from surrounding nuclei and electron clouds except for the contribution from the central anion as

$$V(\mathbf{r}) = \sum_j f_{w_j} \left(-\frac{Z_j}{|\mathbf{r} - \mathbf{r}_{N_j}|} + \int d\mathbf{r}' \frac{\rho_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right), \quad (2)$$

where the first and second terms on the right are the Coulomb potentials produced from the j -th nuclear charge Z_j and electron density ρ_j around the j -th nucleus, respectively. As to the charge weight for the molecular case, $f_{w_j} = 1$. The potential is averaged over the i -th subdomain as

$$V_i = \frac{\int d\mathbf{r}_i V(\mathbf{r}_i)}{\frac{4\pi}{3}(r_{i+1/2}^3 - r_{i-1/2}^3)}, \quad (3)$$

where $r_{i+1/2}$ and $r_{i-1/2}$ are the outer and inner radii of the i -th subdomain. The well depth is relative to the potential at an infinitely distant point from the center. Atomic orbital basis functions are derived in terms of V_i within the well radius. More simply, V_i is averaged with the volume weight as

$$\bar{V} = \sum_i \frac{\frac{4\pi}{3}(r_{i+1/2}^3 - r_{i-1/2}^3)V_i}{\frac{4\pi}{3}r_w^3}, \quad (4)$$

where r_w is the well radius. Practical calculations indicate that results using the above two procedures with and without the average differ little and the number of subdomains does not affect significantly the results.

For the periodic system, well depth is determined by the summation of the Coulomb potential using the Evjen method. The Evjen method first constructs a charge unit cell with the zero total electric charge shown as in Figure 2. The charge weight f_{w_j} for nuclear charge and electron cloud on an atom (anion/cation) is $1/(\text{translation multifold number})$; that is, the charge weight factor in a cell is 1 (one; unity), $1/2$ at a face, $1/4$ on a line and $1/8$ at a corner. The reference level of the well potential in a periodic system is described in the literature [2]. The merit of the Evjen method is that the potential rapidly converges with the increase of the number of neutral charge unit cells.

The SIWB method at first version assigns an anion to the well radius, where anion radii are determined from Pauling's theory using the screened nuclear charges considering Goldschmidt's experimental data, which were compiled as the Shannon radius. In the second version, the SIWB method determined the well radius from the electronic charge density compositions. The

Figure 2. Charge unit cell. The charge weights are also indicated.

definition by the author's SIWB method denoted as R_{eq} was the distance from the point, where electronic charge densities of anion and cation are equal, to the anion nucleus between the nearest neighboring anion and cation. To derive the SIWB well radius via self-consistent iterations, the initial anion well radius is set to the Shannon radius [22–28]. Then, the output of R_{eq} is assigned to the well radius in the next iterations. The final well radius is determined from the converged R_{eq} .

2.2 Finite element approach

The one-electron wave function in the ground state of a diatomic molecule addressed here is axis-symmetric and is conveniently described in a system with cylindrical coordinates (r, z, φ) . The wave equation with the potential $U(r)$

$$\left[-\frac{1}{2}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + U(r)\right]\Psi_i(r) = \varepsilon_i \Psi_i(r), \quad (5)$$

for the wave function $\Psi_i(r) = \psi_i(r, z)\phi_i(\varphi)$ is separated into two equations

$$\left\{-\frac{1}{2}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right) - \frac{m^2}{r^2} + \frac{\partial^2}{\partial z^2}\right] + U(r, z)\right\}\psi_i(r, z) = \varepsilon_i \psi_i(r, z), \quad (6)$$

$$\frac{\partial^2}{\partial \varphi^2} \phi_i(\varphi) = -m^2 \phi_i(\varphi). \quad (7)$$

For s waves with $m = 0$, the equations are simplified to be axis-symmetric. The integral of the kinetic term in the Hamiltonian

$$H_{Ti} = 2\pi \int r dr dz \left\{ \psi_i \left[-\frac{1}{2} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi_i \right] \right\} \quad (8)$$

is rewritten using the partial integral as

$$\begin{aligned} H_{Ti} &= 2\pi \int r dr dz \\ &\times \left\{ \frac{1}{2} \left[\left(\frac{\partial}{\partial x} \psi_i \right) \left(\frac{\partial}{\partial x} \psi_i \right) + \left(\frac{\partial}{\partial y} \psi_i \right) \left(\frac{\partial}{\partial y} \psi_i \right) + \left(\frac{\partial}{\partial z} \psi_i \right) \left(\frac{\partial}{\partial z} \psi_i \right) \right] \right\} \\ &= 2\pi \int r dr dz \left\{ \frac{1}{2} \left[\left(\frac{x}{r} \right)^2 \left(\frac{\partial}{\partial r} \psi_i \right)^2 + \left(\frac{y}{r} \right)^2 \left(\frac{\partial}{\partial r} \psi_i \right)^2 + \left(\frac{\partial}{\partial z} \psi_i \right)^2 \right] \right\} \\ &= 2\pi \int r dr dz \left\{ \frac{1}{2} \left[\left(\frac{\partial}{\partial r} \psi_i \right)^2 + \left(\frac{\partial}{\partial z} \psi_i \right)^2 \right] \right\}. \end{aligned} \quad (9)$$

For the wave function only with the phase dependence along the φ left unconsidered, a basis function allowed is a localized pyramid function centered on a lattice point (r_k, z_l) in the region ranging

$$r_{k-1} \leq r \leq r_{k+1}; z_{l-1} \leq z \leq z_{l+1}, \quad (10)$$

defined as

$$h_{kl}(r, z) = h_k(r)h_l(z), \quad (11)$$

where the composition for $r_{k-1} \leq r \leq r_k$ is

$$h_k(r) = \frac{r - r_{k-1}}{a_r}, \quad (12)$$

and for $r_k \leq r \leq r_{k+1}$,

$$h_k(r) = \frac{r_{k+1} - r}{a_r}. \quad (13)$$

Here,

$$a_r = r_k - r_{k-1} = r_{k+1} - r_k \quad (14)$$

is a lattice spacing along the r axis. Combining the procedure in a corresponding manner for $h_l(z)$ along the z axis, the one-electron wave function is therefore denoted in terms of the basis functions as

$$\psi_i(r, z) = \sum_{kl} \psi_{ikl} h_{kl}(r, z), \quad (15)$$

where ψ_{ikl} are expansion coefficients. The finite element method expresses the wave function in terms of pyramid functions instead of atomic orbitals as in the LCAO.

Boundary conditions for the finite element method are imposed in a natural way. The variational with respect to variables of expansion coefficients is not for variables on the boundary lattice points, that is, the boundary variables do not constitute eigenvectors. Specifying wave function values to vanish at terminal boundaries as

$$\psi_{ik0} = 0, \quad (16)$$

for $l = 0$, for instance, the boundary variables in the Hamiltonian and overlap matrices are dropped.

The axis-symmetric electronic Coulomb potential of a molecule on a lattice point $\mathbf{r}_{kl} = (r_k, z_l, 0)$ contributed from the other composite finite element

$$r_{k'-\frac{1}{2}} \leq r \leq r_{k'+\frac{1}{2}}; z_{l'-\frac{1}{2}} \leq z \leq z_{l'+\frac{1}{2}}; \varphi_{m'-\frac{1}{2}} \leq \varphi \leq \varphi_{m'+\frac{1}{2}}, \quad (17)$$

(with quantities such as $r_{i-1/2}$ and $r_{i+1/2}$ indicating the lower and upper bounds of the finite element), including a lattice point

$\mathbf{r}_{k'l'm'} = (r_k, z_l, \varphi_{m'})$ amounts to

$$V_{Ckl} = \sum_{k'l'm'} \frac{1}{|\mathbf{r}_{k'l'm'} - \mathbf{r}_{kl}|} \rho_{k'l'm'} \Delta V_{k'l'm'}, \quad (18)$$

where $\rho_{k'l'm'}$ is the electronic charge density on a lattice point $\mathbf{r}_{k'l'm'}$ and $\Delta V_{k'l'm'}$ is the volume of the finite element including the lattice point $\mathbf{r}_{k'l'm'}$. Removal of a singularity allows the contribution to the Coulomb potential V_{Ckl} from the specific finite element including the lattice point $\mathbf{r}_{kl}$ to be approximated by the contribution from a sphere with the same volume as the finite element including the lattice point $\mathbf{r}_{kl}$.

3 Results and Discussion

During analyses, the finite element method calculation was first attempted for a specific atom H using the same grid in a cylindrical coordinate system as for calculations of a molecule LiH. The H atom was located at a Cartesian position (0,0,10) in a.u. (Bohr radius), and the section along the z axis was partitioned among three subsections $0 \leq z \leq 10$, $10 \leq z \leq 13.0139$ and $13.0139 \leq z \leq 23.0139$ in a.u. The Cartesian position of (0,0,13.0139) in a.u. was the Li location in the later analysis. The number of lattice points in these subsections including upper and lower bounds were 51, 16 and 51, respectively, with almost constant lattice spacings. The corresponding section along the r axis was $0 \leq r \leq 10$ with 51 lattice points. The number of two-dimensional (2D) lattice points is practical and realistic. Reasonable boundary conditions imposed on wave functions in cylindrical coordinates were values of zero on the edge of the considered domain.

The 1s eigenenergy obtained was -0.5087 Eh and is associated with the relative eigenfunction at $r = 0$ shown with a dotted line in Figure 3, which reasonably reproduced the correct analytical solution (exact solution) indicated with a solid line. The electronic Coulomb potential calculation acquires the 3D

Figure 3. Wave function of the H 1s orbital at $r = 0$ calculated by the finite element method (FEM) with exact solution.

integral, and the number of lattice points minus 10 with respect to φ was 10 at the radial point $r = 0.2$ a.u. and proportional to the radius of the lattice point. The Coulomb potential attained preserved consistency with the analytically estimated values.

Two different LCAO analyses and one finite element approach for an ionic binuclear LiH molecule were then designed to compare these methods. The first is the LCAO analysis (labeled as LCAO-N), which employs the DV LCAO method with a well depth of -1 Eh. The second is the LCAO analysis (labeled as LCAO-SIWB), which is accomplished using the DV method with the SIWB method and leads to a shallower well depth, and the third analysis was the finite element approach. The Cartesian positions of H and Li atoms were (0,0,10) and (0,0,13.0139) in a.u. [24], and the basis set prepared in the LCAO analysis was composed of 1s atomic orbital for the H atom and 1s-2s for the Li atom. The well radius of the anion was determined from the LCAO-SIWB analysis with sequential repetitions until the input well radius converged to the output anion radius R_{eq} . The converged radius and depth of the well were approximately 2.0598 a.u. and -0.199 Eh, respectively. The well radius for LCAO-N calculations was 3.5 a.u. In self-consistent iterations with the finite element method, the system initially has no electron and all starting initial charge density values are zero, while the electron charge densities with a mixing fraction less than or almost 0.4 of the corresponding predicted charge densities were added until the convergence was achieved by iteration.

Figure 4 shows the ratio of the highest occupied wave function 2σ , comprised of the dominant 1s orbital of the H anion, given from LCAO-N to that from the finite element approach, as well as the corresponding ratio from LCAO-SIWB in the

Figure 4. The ratio of the wave function at $r=0$ from the LCAO-SIWB analysis to that from the finite element approach, in addition to the corresponding ratio in the LCAO-N case for a molecule of LiH.

H atom region of $z \leq 10$ at $r=0$ in a.u. along the z axis. All wave functions are normalized to take a value of one (unity) at a position of $z=10$ and $r=0$. This article addresses the wave function in the H anion region of $z \leq 10$, because the emphasis is on the difference in the delocalization of the H 1s atomic orbital basis function between the LCAO-N and LCAO-SIWB methods. Since the dominant component of the 2σ wave function is the H 1s atomic orbital and the influence from Li in the region of $z \leq 10$ is suppressed due to a separate distance from Li, the 2σ wave function in this region has the strong character of the pure basis H 1s atomic orbital. Numerical errors in this H region are reduced owing to the simplicity of the H 1s function, as is confirmed from Figure 3. There is no difference in the treatment of the basis atomic orbitals for the Li cation between the LCAO-N and LCAO-SIWB methods, since no well is added to the potential to generate the basis atomic orbitals for Li. Presently this study does not add a well to the potential for electrons in a cation (positive ion) because such electron can exist stably forming a bound state even in an isolated ion in a vacuum unlike an anion (negative ion). Figure 4 implies that the anion wave function from the LCAO-SIWB analysis can be reproduced from the finite element approach with the better correspondence than that for the LCAO-N case.

The electric dipole moments (electric charge multiplied by internuclear distance) for the Mulliken net charges [21] (not the extended electronic charge density) at the nuclear posi-

tion are 0.06×3.01 (well radius: 2.0598 a.u; well depth: -1.0 Eh), 0.22×3.01 (well radius: 2.0598 a.u; well depth: -0.5 Eh), 0.42×3.01 (well radius: 3.5 a.u; well depth: -1.0 Eh), 0.50×3.01 (well radius: 3.5 a.u; well depth: -0.5 Eh) in a.u. for LCAO-N and 0.48×3.01 for LCAO-SIWB. The results from other approaches are reported in the literatures [29–31].

4 Conclusions

This paper has compared finite element results to those from the LCAO-N method with a well potential depth of -1 Eh only for generation of the anion basis atomic orbitals, and those to the LCAO-SIWB method with a shallower well potential optimized from surrounding nuclei and electron clouds around an anion. The results from the LCAO-SIWB method have closer resemblance to those from the finite-element approach than those from the LCAO-N method.

References

- [1] K. Fukushima, *J. Phys. Soc. Jpn.*, **69**, 1247 (2000). <http://dx.doi.org/10.1143/JPSJ.69.1247> [CrossRef]
- [2] K. Fukushima, *Int. J. Quant. Chem.*, **112**, 44 (2012). <http://dx.doi.org/10.1002/qua.23146>
- [3] K. Fukushima, *Progress in Theoretical Chemistry and Physics*, **26**, 437 (2012). http://dx.doi.org/10.1007/978-94-007-5297-9_24
- [4] K. Fukushima, *Journal of Computer Chemistry, Japan – J-Stage*, **12**, 95 (2013). Freely available website: <http://dx.doi.org/10.2477/jccj.2012-0013>
- [5] H. Wu, L. Zhang, Y. Song, *High Density Data Storage. Principles, Technology and Materials*, Eds. Y. Song and D. Zhu, World Scientific, Singapore (2009) chap. 1. ISBN: 978-981-283-469-0; 978-981-283-470-6
- [6] R. G. Parr, W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford Univ. Press, New York (1989).
- [7] W. Kohn, L. J. Sham, *Phys. Rev.*, **140**, A1133 (1965). [CrossRef]
- [8] J. C. Slater, *Phys. Rev.*, **81**, 385 (1951). [CrossRef]
- [9] D. E. Ellis, G. S. Painter, *Phys. Rev. B*, **2**, 2887 (1970). [CrossRef]
- [10] H. Adachi, M. Tsukada, C. Satoko, *J. Phys. Soc. Jpn.*, **45**, 875 (1978). [CrossRef]
- [11] T. Welzel, K. Ellmer, *J. Vac. Sci. Technol. A*, **30**, 061306 (2012). [CrossRef]
- [12] K. Mitsuke, S. Suzuki, T. Imamura, I. Koyano, *J. Chem. Phys.*, **92**, 6556 (1990). [CrossRef]

- [13] K. Mitsuke, S. Suzuki, T. Imamura, I. Koyano, *J. Chem. Phys.*, **93**, 1710 (1990). [[CrossRef](#)]
- [14] H. M. Evjen, *Phys. Rev.*, **39**, 675 (1932). [[CrossRef](#)]
- [15] F. C. Frank, *Phil. Mag.*, **41**, 1287 (1950).
- [16] C. Kittel, *Introduction to Solid State Physics*, 4th ed., John Wiley and Sons, New York (1971).
- [17] J. M. Ziman, *Principles of the Theory of Solid*, 2nd ed., Cambridge Univ. Press, Cambridge (1972).
- [18] K. Fukushima, *Phys. Rev. D*, **30**, 1251 (1984). [[CrossRef](#)]
- [19] C. M. Bender, K. A. Milton, D. H. Sharp, *Phys. Rev. Lett.*, **51**, 1815 (1983). [[CrossRef](#)]
- [20] A. R. Mitchell, R. Wait, *The Finite Element Method in Partial Differential Equations*, John Wiley & Sons, New York (1977).
- [21] R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955). [[CrossRef](#)]
- [22] R. D. Shannon, C. T. Prewitt, *Acta Cryst. B*, **25**, 925 (1969). [[CrossRef](#)]
- [23] R. D. Shannon, *Acta Cryst. A*, **32**, 751 (1976). [[CrossRef](#)]
- [24] The Chemical Society of Japan, ed., *Handbook of Chemistry: Pure Chemistry*, 2nd-5th eds., Maruzen Pub., Tokyo (until 2004).
- [25] L. Pauling, *J. Am. Chem. Soc.*, **49**, 765 (1927). [[CrossRef](#)]
- [26] L. Pauling, *J. Am. Chem. Soc.*, **51**, 1010 (1929). [[CrossRef](#)]
- [27] V. M. Goldschmidt, *Skrifter Norske Videnskaps-Akad., Oslo, I, Mat-Naturv. Kl.*, 117 (1926).
- [28] V. M. Goldschmidt, *Trans. Faraday Soc.*, **25**, 253 (1929). [[CrossRef](#)]
- [29] P. E. Cade, W. M. Huo, *J. Chem. Phys.*, **45**, 1063 (1966). <http://dx.doi.org/10.1063/1.1671050> [[CrossRef](#)]
- [30] S. Nagaoka, H. Teramae, U. Nagashima, *J. Comput. Chem., Jpn.*, **9**, 177 (2010). [[CrossRef](#)]
- [31] S. Nagaoka, H. Teramae, U. Nagashima, *J. Comput. Chem., Jpn.*, **9**, 241 (2010). [[CrossRef](#)]