Improved tetrahedron method for the Brillouin-zone integration applicable to response functions

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We improve the linear tetrahedron method to overcome systematic errors due to overestimations (underestimations) in integrals for convex (concave) functions, respectively. Our method is applicable to various types of calculations such as the total energy, the charge (spin) density, response functions, and the phonon frequency, in contrast with the Blöchl correction, which is applicable to only the first two. We demonstrate the ability of our method by calculating phonons in MgB2 and fcc lithium.

I. INTRODUCTION

In calculations of periodic systems on the basis of density functional theory (DFT)1, integrals of matrix elements over the Brillouin zone (BZ) are evaluated to obtain various physical quantities of solids including the total energy, the electron (spin) density, the density of states, response functions, and the phonon frequency. Since this integral with respect to the Bloch wave vector \( \mathbf{k} \) is replaced with a summation over a range of points described by a discrete variable \( \mathbf{k} \), approximation schemes employed for this summation can significantly affect the accuracy and computational costs. Accurate integration using a modest number of \( \mathbf{k} \) points is even more important for hybrid-DFT2 and GW approximation3, because in these cases the computational cost is proportional to the square of the number of \( \mathbf{k} \) points, whereas standard semi-local approximations have a linear dependence.

There are two kinds of schemes to perform such an integration over the \( \mathbf{k} \) points, namely, the broadening method4 and the tetrahedron method5. In the broadening method, we replace the delta function with a smeared function which has a finite broadening width; we have to check the convergences about both the broadening width and the number of \( \mathbf{k} \) points to obtain accurate results. In the tetrahedron method, we perform analytical integration in tetrahedral regions covering the BZ with the piecewise linear interpolation of a matrix element. Unlike the broadening method, we have to check the convergence only about the number of \( \mathbf{k} \) points. The tetrahedron method is applied to calculations of susceptibilities, phonon frequency, phonon line width, and the local Green’s function as part of the dynamical mean field theory in the Hubbard model.

However, the tetrahedron method has a drawback; if a matrix element \( A_\mathbf{k} \) is a convex (concave) function of \( \mathbf{k} \), this method systematically overestimates (underestimates) its contribution to the integral due to the linear interpolation involved. Although this can be avoided by using the quadratic interpolation, we cannot perform analytical integration straightforwardly in such a case. The Blöchl correction6 was invented to overcome this issue by utilizing the following two facts: (i) the difference between the linear interpolation integration and that using the quadratic interpolation is approximately proportional to the second derivative of \( A_\mathbf{k} \) integrated over the occupied region; (ii) although \( \partial^2 A_\mathbf{k}/\partial \mathbf{k}^2 \) cannot be evaluated within the framework of linear interpolation, we can perform the volume integral by replacing it with the Fermi surface integration of the first derivative of \( A_\mathbf{k} \) (which can be evaluated by linear interpolation) using the Gauß theorem. Using this method we can reduce the number of \( \mathbf{k} \) points to obtain converged results for total energies and charge densities. However, in the calculation of response functions or phonon frequencies, the integral \( \int_{\epsilon_F<\epsilon} d^3k A_\mathbf{k} / (\epsilon_\mathbf{k} - \epsilon_\mathbf{k}) \) appears, where \( A_\mathbf{k} \) is an arbitrary function of \( \mathbf{k} \). In this case, the Blöchl correction is inapplicable because we cannot perform the Fermi surface integration when \( \partial (A_\mathbf{k} / (\epsilon_\mathbf{k} - \epsilon_\mathbf{k})) / \partial \mathbf{k} \) is singular.

In this work, we develop a new tetrahedron method that is applicable to calculations involving integrations of functions with singularities on the Fermi surfaces. It is constructed by means of a higher-order interpolation and the least square method. We apply our method to the BZ integration in calculations of phonon frequencies based on density functional perturbation theory (DFPT)7. Following that we successfully calculate the frequency of phonons in MgB2 and fcc Li. In contrast, it is difficult to achieve convergence in this calculation using conventional methods because the phonons in these materials couple strongly with electrons in the vicinity of Fermi surfaces.8,9 In Sec. II, we describe our new tetrahedron method in detail after summarizing the conventional linear tetrahedron method and the Blöchl correction. Section III shows how our method improves the convergence about the number of \( \mathbf{k} \) points in the calculation of phonons, followed by the conclusion in Sec. IV.

II. METHOD

In this section, we introduce our new tetrahedron method; we begin with the standard linear tetrahedron method and the Blöchl correction to explain why these methods are not necessarily efficient in calculating re-
response functions such as phonon frequencies.

A. The linear tetrahedron method and its drawbacks

We overview the general procedure of the tetrahedron method and its drawbacks. We calculate the integral

$$\int d^3k A_k B(\epsilon_k), \quad (1)$$

on the basis of the linear tetrahedron method, where $B(\epsilon_k)$ is a function of the orbital energy such as $\theta(\epsilon_F - \epsilon_k)$, $\delta(\epsilon_F - \epsilon_k)$, or $\theta(\epsilon_F - \epsilon_k)/\epsilon_F - \epsilon_k)$. Here, $\theta(x)$ is the Heaviside step function. First, we divide a sub-cell into six tetrahedra (Fig. 1); this sub-cell is partitioned with the uniform $k$-point mesh; for convenience, we number the corners of each tetrahedron from 1 to 4 along specific edges of the sub-cell (see Fig. 1). The contribution of this tetrahedron ($T$) to the integral (1) is

$$6V_T \int_0^1 dx \int_0^{1-x} dy \int_0^{1-x-y} dz A_T(s) B[\epsilon_T(s)], \quad (2)$$

where $s = (x, y, z)$, and

$$A_T(s) \equiv A_{T ij}$$(3)$$

$$\epsilon_T(s) \equiv \epsilon_{T ij}$$(4)

where $k_{ij}$ is the $k$ point of the $i$th corner of $T$. In the linear tetrahedron method, we approximate $A_T$ and $\epsilon_T$ with linear functions:

$$A_{T ij}(s) = A_i (1 - x - y - z) + A_{2 j} x + A_{3 j} y + A_{4 j}, \quad (5)$$

$$\epsilon_{T ij}(s) = \epsilon_i (1 - x - y - z) + \epsilon_{2 j} x + \epsilon_{3 j} y + \epsilon_{4 j}, \quad (6)$$

where $A_i$ and $\epsilon_i$ are the matrix element and the orbital energy at the $i$th corner, respectively. The integration (2) with formulae (3) and (4) is performed **analytically**. However, linear interpolation has a drawback; if the matrix element $A_T(s)$ is a convex function within the tetrahedron $T$, the interpolated function $A_{T ij}(s)$ becomes $A_{T ij}(s) \geq A_T(s)$ in $T$; hence, the integral is systematically overestimated. If $A_T(s)$ is a concave function, the sign of the inequality is reversed (see Fig. 2(a)).

B. The Blöchl correction and its limitation

In the special case that the integral (1) becomes

$$\int d^3k A_k \theta(\epsilon_F - \epsilon_k), \quad (7)$$

we can overcome the drawback of the linear tetrahedron method by considering the curvature of $A_k$ within the framework of the linear interpolation (3). This type of integration appears in the calculations of total energies or charge (spin) densities. In this case, we can evaluate the difference between the integral (7) with the linear interpolation of $A_k$ ($A_{\text{lin}}$) and that with the quadratic interpolation ($A_{\text{quad}}$) as follows. First, we write this difference as

$$\Delta A \equiv A_{\text{quad}} - A_{\text{lin}} = \sum_{ij} \sum_T C_{ij} \left( \frac{\partial^2 A_k}{\partial k_i \partial k_j} \right)_T, \quad (8)$$

where $C_{ij}$ is the form factor describing the shape and the orientation of the tetrahedron as follows

$$C_{ij} = \frac{1}{40} \left[ \sum_{l=1}^{4} (k^T_l)_i \sum_{m=1}^{4} (k^T_m)_j - 4 \sum_{l=1}^{4} (k^T_l)_i (k^T_l)_j \right], \quad (9)$$

and $\langle \cdots \rangle_T$ indicates an integration in the tetrahedron $T$. Now, we replace $\partial^2 A_k/\partial k^2$ with $\partial A_k/\partial k$ because the former cannot be evaluated in the framework of the linear interpolation, but the latter can be. We assume the form factor is a constant over the entire BZ ($C^T_{ij} \approx C_{ij}$), and then we apply the Gauß theorem:

$$\Delta A \approx \sum_{ij} C_{ij} \int_{\epsilon_F < \epsilon_k} d^3k \frac{\partial A_k}{\partial k_i \partial k_j}$$

$$= \sum_{ij} C_{ij} \int_{\epsilon_F = \epsilon_k} d^3k \left( \frac{\nabla_k \epsilon_k}{\nabla_k \epsilon_k} \right) \frac{\partial A_k}{\partial k_j}$$
because we cannot replace \( \nabla A \) response functions and phonon frequencies), the difference (this kind of integration appears in the calculations of response functions and phonon frequencies), the difference associated with the two kinds of interpolation becomes

\[
\Delta A = \sum_{ij} C_{ij} \left( \frac{\partial^2 A_k}{\partial k_i \partial k_j} \right) G(\epsilon_k, \nabla \epsilon_k),
\]

where \( G(\epsilon_k, \nabla \epsilon_k) \) is a complicated function of \( \epsilon_k \) and \( \nabla \epsilon_k \); therefore, we cannot apply the Blöchl correction because we cannot replace \( \partial^2 A_k / \partial k^2 \) with \( \partial A_k / \partial k \) as before. This is due to the presence of the energy denominator; hence, we have to start with another concept to overcome this issue.

### C. A newly improved tetrahedron method applicable to response functions

The systematic error of the tetrahedron method is a result of the linear interpolation. Although we can avoid this problem if we use higher order interpolation, the integral (2) becomes unsolvable analytically. The real question is: how can we improve the linear approximation of the matrix elements? The answer is to employ leveling rather than interpolating (see Fig. 2 b). The procedure is explained below.

1. We construct the \( N \)th polynomial \( A^N_k(s) \) from \( A_k \) and \( k \) using the corners of a tetrahedron \( T \) and some additional surrounding points for sampling.

2. We fit a linear function

\[
A^L_{T \text{SM}}(s) = \tilde{A}_1(1-x-y-z) + \tilde{A}_2x + \tilde{A}_3y + \tilde{A}_4z
\]

into \( A^N_k(s) \) through the least square method (LSM); that is to say, we solve

\[
\frac{\partial}{\partial A_k} \int_0^1 dx \int_0^{1-x} dy \int_0^{1-x-y} dz \times |A^N_k(s) - A^L_{T \text{SM}}(s)|^2 = 0.
\]

3. We apply the same procedure to \( \epsilon_k \), and obtain \( \epsilon^L_{T \text{SM}}(s) \).

4. We evaluate integral (2) replacing \( A_T(s) \) and \( \epsilon_T(s) \)

with \( A^L_{T \text{SM}}(s) \) and \( \epsilon^L_{T \text{SM}}(s) \), respectively.

5. We repeat the above steps for all tetrahedra.

Although the approximated matrix element \( A^L_{T \text{SM}}(s) \) is discontinuous at boundaries of tetrahedra (see Fig. 2 b)), it is of no concern because we are interested only in the integrated value.

![Fig. 3. Points for constructing a third order interpolation function (parallel stereogram). Red points denote the corners of \( T \). The blue and green points are explained in Table I.](image)

### TABLE I. Points for constructing a third order interpolation function

| Nearest neighbor points on extended lines of each edge of \( T \) (green balls in Fig. 3) |
|---|
| \( k_5 = 2k_1 - k_2 \) | \( k_9 = 2k_1 - k_3 \) | \( k_{13} = 2k_1 - k_4 \) |
| \( k_6 = 2k_2 - k_3 \) | \( k_{10} = 2k_2 - k_4 \) | \( k_{14} = 2k_2 - k_1 \) |
| \( k_7 = 2k_3 - k_4 \) | \( k_{11} = 2k_3 - k_1 \) | \( k_{15} = 2k_3 - k_2 \) |
| \( k_8 = 2k_4 - k_1 \) | \( k_{12} = 2k_4 - k_2 \) | \( k_{16} = 2k_4 - k_3 \) |

Remaining corners of tetrahedra that share surfaces with \( T \) (blue balls in Fig. 3).

| \( k_{17} = k_1 - k_2 + k_3 \) | \( k_{18} = k_1 - k_2 + k_4 \) |
| \( k_{19} = k_2 - k_3 + k_4 \) | \( k_{20} = k_3 - k_4 + k_1 \) |

### D. Implementation

We use a third order polynomial \( A^3_T(s) \) as \( A^N_k(s) \) in our implementation. The sampling points used to construct \( A^3_T(s) \) are the corners of the tetrahedron \( T \) (4 points) and the other 16 points given in Table I and Fig. 3. As a result, \( A^3_T(s) \) becomes

\[
A^3_T(s) = \frac{A_1}{2} u(u+1)(2-u) + \frac{A_2}{2} x(x+1)(2-x) + \frac{A_3}{2} y(y+1)(2-y) + \frac{A_4}{2} z(z+1)(2-z)
\]

\[
- u^2 x^2 (2A_5 + A_{14}) - \frac{x^2 y}{6} (2A_6 + A_{15})
\]

\[
- u^2 y^2 (2A_7 + A_{16}) - \frac{z^2 u}{6} (2A_8 + A_{13})
\]

\[
- u^2 z^2 (2A_9 + A_{11}) - \frac{x^2 z}{6} (2A_{10} + A_{12})
\]

\[
- y^2 u^2 (2A_{11} + A_9) - \frac{z^2 x}{6} (2A_{12} + A_{10})
\]

\[
- u^2 z^2 (2A_{13} + A_8) - \frac{x^2 u}{6} (2A_{14} + A_5)
\]

\[
- y^2 x^2 (2A_{15} + A_6) - \frac{z^2 y}{6} (2A_{16} + A_7)
\]

\[
+ (A_2 + A_4)xz(u + y) + (A_1 + A_3)uy(x + z)
\]
where \( w = 1 - x - y - z \). By substituting it into (14), we obtain \( A_i^{SM}(s) \):

\[ A_i = \sum_{j=1}^{20} P_{ij} A_{kj}, \]

where

\[ P = (P^{(1)}, P^{(2)}, P^{(3)}, P^{(4)}, P^{(5)}), \]

\[ P^{(1)} = \frac{1}{1260} \begin{pmatrix} 1440 & 0 & 30 & 0 \\ 0 & 1440 & 0 & 30 \\ 30 & 0 & 1440 & 0 \\ 0 & 30 & 0 & 1440 \end{pmatrix}, \]

\[ P^{(2)} = \frac{1}{1260} \begin{pmatrix} -38 & 7 & 17 & -28 \\ -28 & -38 & 7 & 17 \\ 17 & -28 & -38 & 7 \\ 7 & 17 & -28 & -38 \end{pmatrix}, \]

\[ P^{(3)} = \frac{1}{1260} \begin{pmatrix} -56 & 9 & -46 & 9 \\ 9 & -56 & 9 & -46 \\ -46 & 9 & -56 & 9 \\ 9 & -46 & 9 & -56 \end{pmatrix}, \]

\[ P^{(4)} = \frac{1}{1260} \begin{pmatrix} -18 & -18 & 12 & -18 \\ -18 & -18 & 12 & -18 \\ 12 & -18 & -18 & 12 \\ -18 & 12 & -18 & 12 \end{pmatrix}, \]

\[ P^{(5)} = \frac{1}{1260} \begin{pmatrix} -18 & -18 & 12 & -18 \\ -18 & -18 & 12 & -18 \\ 12 & -18 & -18 & 12 \\ -18 & 12 & -18 & 12 \end{pmatrix}. \]

We go through the same procedure for the orbital energy \( \epsilon_k \).

We can consider this procedure in a different way: when we calculate the contribution from a tetrahedron, we use the linear tetrahedron method after we have replaced matrix elements and orbital energies with those given in (16). Using this idea, we represent the integration (1) as

\[ \int d^3k A_k B(\epsilon_k) = \sum_k A_k w_k, \]

where \( w_k \) is calculated as follows:

1. We divide the BZ into tetrahedra.
2. We calculate effective orbital energies as

\[ \bar{\epsilon}_i = \sum_{j=1}^{20} P_{ij} \epsilon_{kj} \]

for the corners of each tetrahedron.

3. We calculate the effective weight \( \bar{w}_T^i \) using the standard linear tetrahedron method with the effective orbital energy (23).

4. \( w_k \) is calculated as

\[ w_k = \sum_{T=1}^{4} \sum_{i=1}^{20} P_{ij} \bar{w}_T^i \delta(k - k_f^T). \]

III. COMPARISON WITH OTHER INTEGRATION SCHEMES FOR ACTUAL CALCULATIONS

We implement our method in an \emph{ab initio} electronic structure calculation code \textsc{Quantum Espresso} which uses plane waves to represent Kohn-Sham (KS) orbitals. Then, we test the effectiveness of the method through calculations of phonons in two systems, MgB\(_2\) and fcc lithium at a high pressure (20 GPa), based on DFT\(^{13}\) (Appendix A).

Magnesium diboride has the highest \( T_c \) (about 40 K) out of the known phonon-type superconductors. Many \emph{ab initio} studies have been performed since it was discovered\(^{12,15,19}\), revealing that the high \( T_c \) is a result of the strong interaction between intra-layer vibrations of B atoms and their covalent bonding orbitals (\( \sigma \) bands) (Fig. 4). This strong coupling also softens phonon frequencies due to the screening of the ion-ion interaction; this screening occurs due to linear responses of \( \sigma \) electrons in the vicinity of the Fermi surfaces. We have to evaluate these responses accurately to determine the phonon frequencies precisely. Lithium exhibits a monatomic \( fcc \) structure at pressures between 7.5 and 39 GPa\(^{20}\) in this phase it becomes a superconductor. Its \( T_c \) increases with pressure up to 30 GPa\(^{21,23}\) because of the growth of the electron-phonon interaction. The lower transverse acoustic mode at \( q \approx \Gamma K \) couples with electrons most strongly in this material\(^{13}\). In this test, we consider the phonons of \( fcc \) Li at a pressure of 20 GPa.
We use norm-conserving pseudopotential\cite{24} in calculations of MgB$_2$: the cutoff energy of plane waves is set to 50 Ry. In the calculations of fcc lithium, we use an ultrasoft pseudopotential\cite{26} We treat the electrons in the 1s orbitals as valence electron\cite{27} and employ a cutoff energy of 80 Ry. In both of these applications, we use the GGA-PBE functional\cite{26} and the first-order Hermite-Gaussian function\cite{26} for broadening. We apply our method to the calculation of the frequency of the intra-layer vibrational mode of B atoms at the A point in the BZ (Fig. 5 top left). The result of the improved tetrahedron method converges faster than that of the linear tetrahedron method: it converges with approximately $12^3$ $k$ points. If we use a broadening method with a small broadening width (0.01 Ry), the result converges at an unrealistically large number of $k$ points (about $50^3$ $k$ points). On the other hand, using large broadening widths (0.03 Ry and 0.06 Ry), convergence occurs at a lower number of $k$ points. However, results are far away from the one converged about the broadening width: The complicated dependence of the convergence on the broadening width is shown in the top-right panel of Fig. 5. The result cannot be represented by a simple function, so it is difficult to extrapolate to a broadening width of zero.

The bottom left panel of Fig. 5 shows the $k$ convergence of the lower transverse acoustic mode at the $K$ point in the BZ for fcc Li at 20 GPa calculated with the different integration schemes. Our method achieves convergence very quickly; it requires only $16^3$ $k$ points. In this system, the result of the broadening method is very sensitive to the broadening width; the error due to broadening is more than 25% at a width of 0.05 Ry; hence, the broadening method is not suitable for this calculation.

We will show how the accuracy of the phonon calculations affects the prediction of the superconducting transition temperature within the framework of the following McMillan formula\cite{29,30}:

$$T_C = \frac{\omega_{0 \log}}{1.2} \exp \left( \frac{-1.04(1 + \lambda)}{\lambda - \mu^* (1 + 0.62\lambda)} \right),$$

(25)

Here,

$$\lambda = \sum_{q\nu k n\nu} \frac{2}{D(\epsilon_F)\omega_{q\nu}} \left| g_{n k n' k + q}^{q\nu} \right|^2 \delta(\epsilon_{n k} - \epsilon_F) \delta(\epsilon_{n' k + q} - \epsilon_F)$$

(26)

and

$$\log(\omega_{0 \log}) = \frac{1}{\lambda} \sum_{q\nu k n\nu} \frac{2}{D(\epsilon_F)\omega_{q\nu}} \log(\omega_{q\nu})$$

$$\times \left| g_{n k n' k + q}^{q\nu} \right|^2 \delta(\epsilon_{n k} - \epsilon_F) \delta(\epsilon_{n' k + q} - \epsilon_F),$$

(27)

where $\omega_{q\nu}$ is the phonon frequency with the wave number $q$ and the branch $\nu$, $\epsilon_{nk}$ is the KS eigenvalue with the wave number $k$ and the band index $n$, and $D(\epsilon_F)$ is the density of states per spin at the Fermi energy. The electron-phonon coupling constant $g_{n k n' k + q}^{q\nu}$ is written in the form

$$g_{n k n' k + q}^{q\nu} = \sum_{\tau \alpha} \frac{(\eta_{q\nu})_{\tau \alpha}}{M_{\tau\alpha}} \left\langle n', k + q \mid \frac{\delta v_S}{\delta R_{\tau\alpha}(q)} \mid n, k \right\rangle,$$

(28)

where $M_{\tau\alpha}$ is a mass of an ion, $(\eta_{q\nu})_{\tau \alpha}$ is the unit displacement pattern of the phonon $(q, \nu)$, $(n,k)$ is the KS orbital, and $\delta v_S / \delta R_{\tau\alpha}(q)$ is the linear response of the KS potential with respect to the distortion of the wave number $q$: $\tau$ and $\alpha$ are indices of an ion in the unit cell and a direction in the Cartesian coordinate, respectively. Although there are more precise methods to calculate $T_C$ such as density functional theory for...
superconductors, we use this simple formula because we are only interested in changes in the results due to the \( k \) integration in the phonon calculations.

To evaluate the integrals in Eq. (26) and Eq. (27), we use the linear tetrahedron method with a \( q \) grid of \( 6 \times 6 \times 4 \) (8 \( \times \) 8 \( \times \) 8) and a \( k \) grid of 24 \( \times \) 24 \( \times \) 18 \( (32 \times 32 \times 32) \) for MgB\(_2\) (fcc Li), respectively. Additionally, we calculate each \( \omega_q \) and \( \delta w / \delta R_{\rho}(q) \) with different \( k \) grids and different \( k \) integration schemes.

Figure 6 shows the result of \( \lambda \), \( \omega_{\log} \), and \( T_C \) from the McMillan’s formula (\( \mu' = 0.1 \)); in both the MgB\(_2\) and Li cases, we obtain very fast \( k \) convergence using our method. Comparing the \( k \) converged result of our method to that of the broadening method with a width of 0.05 Ry, we can see a large overestimate of the phonon frequencies occurs when the broadening method is used, resulting in an underestimated \( \lambda \) and an overestimated \( \omega_{\log} \). Moreover, speeds of convergences about the broadening width for calculations of the \( \lambda \) and \( \omega_{\log} \) are very slow; these results have not reach the convergence even for the broadening width of 0.01 Ry; if we use smaller broadening width (such as 0.005 Ry), we need an unrealistic number of \( k \) points to obtain the \( k \)-converged result.

**IV. CONCLUSION**

We introduced an improvement to the tetrahedron method based on the third order interpolation and the least square method that reduces the number of \( k \) points required to obtain converged results of the BZ integrations. Our method is applicable to various kinds of \( k \)-integration; in particular, it is efficient for calculations of phonons and response functions because the associated computational costs are large and the B\( \ddot{o} \)chli correction is not applicable to these calculations. We demonstrated this effectiveness through calculations of phonon frequencies in MgB\(_2\) and fcc Li.

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**Appendix A: Calculation of weights for DFPT**

The integration weights for the DFPT calculations of phonon frequencies are different from those of the total energy, \( \theta(\epsilon_\nu - \epsilon_{nk}) \), or the density of states, \( \delta(\epsilon - \epsilon_{nk}) \). They are

\[
W^{(1)}_{n\nu',k} = \frac{\theta(\epsilon_{n'k+q} - \epsilon_\nu)\theta(\epsilon_\nu - \epsilon_{nk})}{\epsilon_{nk} - \epsilon_{n'k+q}}
\]

\[
W^{(2)}_{n\nu',k} = \theta(\epsilon_\nu - \epsilon_{nk})\theta(\epsilon_{nk} - \epsilon_{n'k+q}).
\]

In integrations with weights that contain products of two step functions, only regions where both Heaviside functions become 1 contribute to the results; therefore, we divide the tetrahedra two times to cut out these regions (Fig. 7). We will explain how to calculate \( W^{(1)}_{n\nu',k} \).

1. We divide a sub-cell into six tetrahedra.
2. We cut out one or three tetrahedra \( T' \) where \( \theta(\epsilon_\nu - \epsilon_{nk}) = 1 \) from tetrahedron \( T \) and evaluate \( \epsilon_{nk}, \epsilon_{n'k+q} \) at the corners of \( T' \) as

\[
\epsilon_{T'i} = \sum_{j=1}^{4} F_{ij}(\epsilon_\nu - \epsilon_{T1}, \cdots, \epsilon_\nu - \epsilon_{T4})\epsilon_{Tj},
\]
through linear interpolation (Appendix B). Here \( \epsilon_{T1}, \ldots, \epsilon_{T4} \) and \( \epsilon'_{T1}, \ldots, \epsilon'_{T4} \) are \( \epsilon_{nk} \) and \( \epsilon_{n'k+q} \), respectively, on the corners of \( T \), where \( \epsilon_{T1} \leq \epsilon_{T2} \leq \epsilon_{T3} \leq \epsilon_{T4} \).

3. We cut out one or three tetrahedra \( T'' \) where \( \theta(\epsilon_{n',k+q} - \epsilon_F) = 1 \) from tetrahedron \( T' \). The orbital energies are calculated as

\[
\epsilon_{T''} = \sum_{j=1}^{4} F_{ij} (\epsilon'_{T'1} - \epsilon_F, \ldots, \epsilon'_{T'4} - \epsilon_F) \epsilon_{T''j}. \tag{A4}
\]

4. The weights of the corners of \( T'' \) are (Appendix C)

\[
W_{T''}^{(1)} = -V_{T''} \sum_{j=1, j \neq i}^{4} d_j (\ln d_j - \ln d_i) \prod_{k=1, k \neq j}^{4} (d_j - d_k), \tag{A5}
\]

where \( d_i = \epsilon'_{T''i} - \epsilon_{T''i} \).

5. We calculate the weights of the corners of \( T'' \) from those of \( T'' \).

\[
W_{T''}^{(1)} = \sum_{j=1}^{4} F_{ji} (\epsilon'_{T'1} - \epsilon_F, \ldots, \epsilon'_{T'4} - \epsilon_F) W_{T''}^{(1)} \tag{A6}
\]

6. We calculate the weights of the corners of \( T \) from those of \( T'' \).

\[
W_{T}^{(1)} = \sum_{j=1}^{4} F_{ji} (\epsilon_F - \epsilon_{T1}, \ldots, \epsilon_F - \epsilon_{T4}) W_{T''}^{(1)}. \tag{A7}
\]

7. Finally, we sum up the contributions from all tetrahedra.

\[
W_{T''}^{(1)} = \sum_{T=1}^{6N_k} \sum_{i=1}^{4} W_{T_i}. \tag{A8}
\]

**FIG. 7.** Flow of the calculation of weights. We divide the tetrahedra two times to cut out regions where two Heaviside functions become one.

**FIG. 8.** How to divide a tetrahedron in the case of \( \epsilon_1 \leq \epsilon_2 \) (left), \( \epsilon_2 \leq \epsilon_3 \) (center), and \( \epsilon_3 \leq \epsilon_4 \) (right).

**Appendix B: How to divide a tetrahedron**

We will explain how to cut out tetrahedra \( T' \) in the case of \( \theta(\epsilon) = 1 \) from tetrahedron \( T \). We represent \( \epsilon_{nk} \) at the corners of \( T \) as \( \epsilon_1, \ldots, \epsilon_4 \), where \( \epsilon_1 \leq \epsilon_2 \leq \epsilon_3 \leq \epsilon_4 \). We define \( a_{ij} = -\epsilon_j / (\epsilon_i - \epsilon_j) \). In all cases

\[
V_{T'} = V_T |\det(F)|. \tag{B1}
\]

1. \( 0 \leq \epsilon_1 \):

We cut out no tetrahedra because \( \theta(\epsilon) \) becomes 1 over the entire tetrahedron in this case.

\[
F = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}. \tag{B2}
\]

2. \( \epsilon_1 \leq 0 < \epsilon_2 \):

Three tetrahedra are cut out (Fig. 8 left).

\[
(a) \quad F = \begin{pmatrix} a_{12} & a_{21} & 0 & 0 \\ a_{13} & 0 & a_{31} & 0 \\ a_{14} & 0 & 0 & a_{41} \\ 0 & 0 & 0 & 1 \end{pmatrix}. \tag{B3}
\]

\[
(b) \quad F = \begin{pmatrix} a_{12} & a_{21} & 0 & 0 \\ a_{13} & 0 & a_{31} & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}. \tag{B4}
\]

\[
(c) \quad F = \begin{pmatrix} a_{12} & a_{21} & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}. \tag{B5}
\]

3. \( \epsilon_2 \leq 0 < \epsilon_3 \):

...
Three tetrahedra are cut out (Fig. 8 center).

(a) \[ F = \begin{pmatrix} a_{13} & 0 & a_{31} & 0 \\ a_{14} & 0 & 0 & a_{41} \\ 0 & a_{24} & 0 & a_{42} \\ 0 & 0 & 0 & 1 \end{pmatrix} \] (B6)

(b) \[ F = \begin{pmatrix} a_{13} & 0 & a_{31} & 0 \\ 0 & a_{23} & a_{32} & 0 \\ 0 & a_{24} & 0 & a_{42} \\ 0 & 0 & 0 & 1 \end{pmatrix} \] (B7)

(c) \[ F = \begin{pmatrix} a_{13} & 0 & a_{31} & 0 \\ 0 & a_{23} & a_{32} & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \] (B8)

4. \( \epsilon_3 \leq 0 < \epsilon_4 \):
One tetrahedron is cut out (Fig. 8 right).

\[ F = \begin{pmatrix} a_{14} & 0 & 0 & a_{41} \\ 0 & a_{24} & 0 & a_{42} \\ 0 & 0 & a_{34} & a_{43} \\ 0 & 0 & 0 & 1 \end{pmatrix} \] (B9)

Appendix C: Calculation of \( W_{T''}^{(1)} \)

We represent the matrix elements at the corners of the tetrahedron as \( f_1, \ldots, f_4 \). We evaluate the integral

\[ \left\langle \frac{A}{d} \right\rangle_{T''} = \int_{T''} d^3k \frac{A_k}{d_k} \] (C1)

using linear interpolation to obtain

\[ A_{T''} \approx 6 V'' \int_0^1 dx \int_0^{1-x} dy \int_0^{1-x-y} dz \]
\[ \times \frac{A_1 + (A_2 - A_1)x + (A_3 - A_1)y + (A_4 - A_1)z}{d_1 + (d_2 - d_1)x + (d_3 - d_1)y + (d_4 - d_1)z} \]
\[ \equiv \sum_{i=1}^4 A_i W_{T''i}. \] (C2)

where

\[ W_{T''i} = 6 V'' \int_0^1 dx_1 \int_0^1 dx_2 \int_0^1 dx_3 \int_0^1 dx_4 \]
\[ \times \frac{x_i^2 (x_1 + x_2 + x_3 + x_4 - 1)}{d_1 x_1 + d_2 x_2 + d_3 x_3 + d_4 x_4}. \] (C3)

This in turn yields (A5).

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