

Approximate occupation functions for density-functional calculations

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The density-functional free energy can be written in a form that is stationary with respect to variations in the occupation function. For this reason it is useful to look for approximate occupation functions that are sufficiently close to the Fermi function that accuracy is not compromised and yet have advantages for computation. From a computational point of view it is useful to reduce the number of poles of the occupation function in the upper half of the complex energy plane and to locate the poles as far from the real axis as possible. A family of approximate occupation functions that economize computation is introduced. Their properties are discussed and illustrated for a model system. [S0163-1829(97)04644-4]

I. INTRODUCTION

In electronic structure calculations based on Green-function approaches, it is common to circumvent integrals over real energy by analytic continuation into the complex energy plane. The Green function has no poles in the upper half plane so the integration path over energy (that at zero temperature typically extends from the energy, $\epsilon = -\infty$, to the Fermi energy, $\epsilon = \mu$) can be deformed upward into the complex energy plane. This deformation moves the calculation of, for example, the density of states to complex energies where it is a smooth function. This procedure greatly reduces the number of required integration mesh points. Unfortunately the integration contour must return to the real axis at $\epsilon = \mu$ and the integration mesh must be finer along this last segment. Another important advantage of having a finite imaginary part to the energy is that the Koringa-Kohn-Rostoker, KKR, matrix whose inversion accounts for the vast majority of the computation time is much better conditioned at complex energies and is amenable to rapid inversion by iterative techniques.¹

At finite temperature the Green function remains analytic in the upper half plane. Integration over energy extends from $\epsilon = -\infty$ to $\epsilon = +\infty$, but the required integrals to determine the electron density, eigenvalue sum, number of electrons, and the electron-hole entropy involve products of the Green function and the Fermi distribution function. The Fermi function does have poles in the upper half plane. When the integration over complex energy along a contour, $\epsilon = Re^{i\phi}$ where $R \rightarrow \infty$, vanishes one can utilize the residue theorem and evaluate the integral over the real energy by summing over the residues at each of the poles of the Fermi function. (As discussed below the entropy involves branch cuts that preclude deforming the integration contour to infinity.) We emphasize that in this paper the temperature and entropy refer to the electronic degrees of freedom. The nuclear positions and occupations may be at $T=0$ or some other temperature, in which case the formalism described here would apply to calculation of the free energy in the Born-Openheimer approximation. It is evident that the positions and number of poles of the occupation function determine the amount of computation required. Of course the Fermi occupation function is known and is fixed for a given tem-

perature so there appears to be no flexibility in the nature of the poles. However, the free energy is stationary with respect to variation of the occupation function. This allows us to make small modifications to the occupation function without degrading the free energy.² Beyond this, we are able to make large changes in the occupation function over energy ranges where the density of states is zero. The free energy is obviously independent of changes in the occupation function over these ranges. Furthermore, the difference in free energy between two systems is independent of changes in the occupation function over those energies at which the density of states of the two systems is the same.

Further freedom is attainable because different approximations to the occupation function can be used for different contributions to the charge, i.e., valence and core, single site and multiple scattering, or *s*, *p*, *d*, and *f* orbitals.

II. FREE-ENERGY FUNCTIONAL

The statement that “the free energy is stationary with respect to the occupation function” is actually inaccurate. Only certain forms of the expression for the free energy have this property. The importance of using a free-energy expression that is variational in the occupation function has been recently emphasised by Wildberger *et al.*⁵ However, the cited literature proposes a final expression that is in fact not variational. To clarify this point and to demonstrate the way in which any algorithm for the number of electrons *N* as a function of the chemical potential μ determines the free energy, we use the thermodynamic relation³ between the grand potential Ω and the number of electrons to derive the free energy,

$$\frac{\partial \Omega}{\partial \mu} = -N. \quad (1)$$

Within the Kohn-Sham scheme of density-functional theory, *N* is given by $N = \int_{-\infty}^{\infty} d\epsilon n(\epsilon) f(\epsilon - \mu)$, where $n(\epsilon)$ is the density of states. Integrating over the chemical potential and adding μN the free energy is obtained:

$$F = \mu N - \int_{-\infty}^{\mu} d\mu \int_{-\infty}^{\infty} d\epsilon n(\epsilon) f(\epsilon - \mu). \quad (2)$$

This expression is manifestly first order in the occupation function f . Using an identity relating $n(\epsilon)$ to the integrated density of states, $N(\epsilon) = \int_{-\infty}^{\epsilon} d\epsilon n(\epsilon)$,

$$f(\epsilon)n(\epsilon) = \frac{d(Nf)}{d\epsilon} + \frac{d(Nf)}{d\mu} - f \frac{dN}{d\mu} \quad (3)$$

and using $\delta N / \delta v = -\rho$ and $v = \delta(U + E_{xc}) / \delta \rho$ we arrive at the more familiar form,

$$\begin{aligned} F &= \mathbf{N}\mu - \int_{-\infty}^{\infty} d\epsilon Nf + \int_{-\infty}^{\mu} d\mu \int_{-\infty}^{\infty} d\epsilon \int_0^{\infty} d\mathbf{r} \frac{\delta N}{\delta v} \frac{dv}{d\mu} \\ &= \mathbf{N}\mu - \int_{-\infty}^{\infty} d\epsilon Nf - \int_0^{\infty} d\mathbf{r} \rho(\mathbf{r})v(\mathbf{r}) + U(\rho) + E_{xc}(\rho), \end{aligned} \quad (4)$$

where U and E_{xc} are the electron-electron plus electron-ion energy and the exchange-correlation energy, respectively. This form fits well with techniques that use the Lloyd^{4,5} integrated density of states formula to accelerate the angular momentum convergence of the “band” energy. It is not, however, the best form to use in conjunction with approximate occupation functions, because it is not stationary in f . It should be noted that even if the exact Fermi function is used, any energy integration mesh used to construct the electron density or the eigenvalue sum implies an implicit approximation to f . The approach in Ref. 5 is to converge the integration mesh. This convergence is reached fairly rapidly because the integration path is far from the real axis in the region where the Green function varies smoothly with energy. We avoid the issue of converging the energy integral by approximating the occupation function and employing an extremal free energy. In order to obtain a form stationary in f we must integrate by parts using the identity,

$$(\epsilon - \mu) \frac{df}{d\epsilon} = k_B T \frac{d}{d\epsilon} [f \ln f + (1-f) \ln(1-f)], \quad (5)$$

valid for the Fermi function, $f_F = (e^{(\epsilon - \mu)/k_B T} + 1)^{-1}$. Proceeding, we obtain an expression for F with the desired stationarity,⁶⁻⁹

$$\begin{aligned} F[\rho] &= \int_{-\infty}^{\infty} d\epsilon \epsilon f(\epsilon - \mu) n(\epsilon) - \int d\mathbf{r} \rho v + U[\rho] + E_{xc}[\rho] \\ &\quad + \mu \left[\mathbf{N} - \int_{-\infty}^{\infty} d\epsilon f(\epsilon - \mu) n(\epsilon) \right] \\ &\quad + k_B T \int_{-\infty}^{\infty} d\epsilon n(\epsilon) \{ f(\epsilon - \mu) \ln[f(\epsilon - \mu)] \\ &\quad + [1 - f(\epsilon - \mu)] \ln[1 - f(\epsilon - \mu)] \}. \end{aligned} \quad (6)$$

The fact that the free energy is stationary with respect to ρ makes it easy for the reader to verify that the above expression is stationary with respect to f . At this point we turn our attention to approximate forms for f that can take advantage of this stationarity.

III. APPROXIMATE OCCUPATION FUNCTIONS

It was demonstrated in a previous paper² that functions with a limited number of poles can accurately reproduce f_F . The form described in this earlier work was motivated by replacing the exponential in f_F by the well known approximation $e^x \approx (1 + x/N)^N$ for large N , obtaining

$$f_N^1(z - \mu) = \frac{1}{\left(1 + \frac{z - \mu}{Nk_B T}\right)^N + 1}. \quad (7)$$

Here the subscript N indicates the number of poles, and the superscript 1 is the value of a parameter that will be defined later. f_N^1 can also be written less compactly in terms of its poles in the upper half plane,

$$f_N^1(\epsilon - \mu) = \frac{1}{2} - (\epsilon - \mu)/k_B T \sum_{j=1}^{N/2} \frac{\frac{(\epsilon - \mu)}{Nk_B T} + 2}{\left[(\epsilon - \mu)/k_B T + N \left(1 - \cos \pi \frac{2j-1}{N} \right) \right]^2 + \left[N \sin \pi \frac{2j-1}{N} \right]^2}. \quad (8)$$

This can be compared with the corresponding expression for the exact function,

$$\begin{aligned} f_F(\epsilon - \mu) &= \frac{1}{2} - (\epsilon - \mu)/k_B T \\ &\quad \times \sum_{j=1}^{\infty} \frac{2}{[(\epsilon - \mu)/k_B T]^2 + [\pi(2j-1)]^2}. \end{aligned} \quad (9)$$

An obvious distinction between f_N^1 and f_F is that the former has $N/2$ poles and the latter has an infinite number of poles. The Fermi function converges slowly in the number of poles included in Eq. (9) so it is not feasible to simply truncate the sum at a convenient number. One possible approach for con-

structing approximate occupation functions would be to select a number of poles and then optimize the position and residue of each pole with respect to agreement with f_F over a specified range. Optimization for a particular type of density of states in order to reproduce the band energy would be possible. This might reduce computation time, but one would have to be mindful of the fact that energies calculated with different occupation functions probably cannot be used to evaluate energy differences. An approach based on such an optimization of poles and residues provides the most general set of possible occupation functions. In this work we investigate a more limited set generated by rational polynomial

approximation of the exponential that appears in f_F . Several criteria will be imposed to reduce the number of candidate expressions to an even smaller set that can be described by the number of poles in the upper half plane and the maximum deviation of the occupation function from zero at positive energies.

To simplify the presentation we will measure energy in multiples of $k_B T$ from the chemical potential. Note that

$$\begin{aligned} f_F^{-1} - 1 &= e^x = \lim_{N \rightarrow \infty} \left(1 + \frac{x}{N} \right)^N, \\ &= \lim_{N \rightarrow \infty} \frac{1}{\left(1 - \frac{x}{N} \right)^N} = \lim_{N \rightarrow \infty} \frac{1}{\left(1 + \frac{x}{N} \right)^{-N}}, \\ &= \lim_{N \rightarrow \infty} \prod_i (1 + \alpha_i x)^{\beta_i N} \quad \text{if} \quad \sum_i \alpha_i \beta_i = 1. \end{aligned} \quad (10)$$

We take N to be finite (roughly between 8 and 64) and restrict ourselves to choices of α_i and β_i that lead to functions that grow rapidly at large x . It is therefore convenient to separate the factors in the equation above according to the sign of β_i :

$$f_F^{-1} - 1 = e^x = \lim_{N \rightarrow \infty} \frac{(1 + \alpha_1 x)^{\beta_1 N} (1 + \alpha_2 x)^{\beta_2 N} \dots}{(1 + \gamma_1 x)^{\delta_1 N} (1 + \gamma_2 x)^{\delta_2 N} \dots}, \quad (11)$$

where $\beta_i > 0$, $\delta_i > 0$, and $N \sum_i \beta_i \gg N \sum_i \delta_i$. The poles of f_F occur when this fraction is equal to -1 . If, by raising the fraction to a power, it is converted into the ratio of two low order polynomials the roots can be found by standard techniques. If we restrict our selection to choices that allow the poles of the occupation function to be determined by the solution of a quadratic equation the fraction must be reduced to the ratio of a quadratic to a linear function. We are therefore limited to the form

$$f_N^{\gamma-1} - 1 \approx \frac{\left[1 + x \left(\frac{1+\gamma}{2N} \right) \right]^N}{\left[1 - x \left(\frac{1-\gamma}{N} \right) \right]^{N/2}}, \quad (12)$$

$$\gamma = 1 - 2 \left[\left(\frac{1 - f_{\max}}{f_{\max}} \right)^{2/N} + 1 \right]^{-1/2}, \quad (13)$$

$$f_{\max} = \frac{1}{[4(1-\gamma)^{-2} - 1]^{N/2} + 1}. \quad (14)$$

We restrict N to be a multiple of 4; other values of N give occupation functions that are either greater than 1 or negative over some ranges. This approximation gives an occupation function with a maximum at $x = 4N/(1-\gamma^2)$ of height f_{\max} . It has a minimum of zero at $x = N/(1-\gamma)$ and a maximum of one at $x = -2N/(1+\gamma)$. In the limit $\gamma \rightarrow 1$, f becomes the original approximation given in Eq. (7). In Fig. 1, for the case of 16 poles the positions of the poles in the upper half plane are shown, for even values of $N\gamma$, ranging from zero to N . The corresponding functions on the real axis are com-

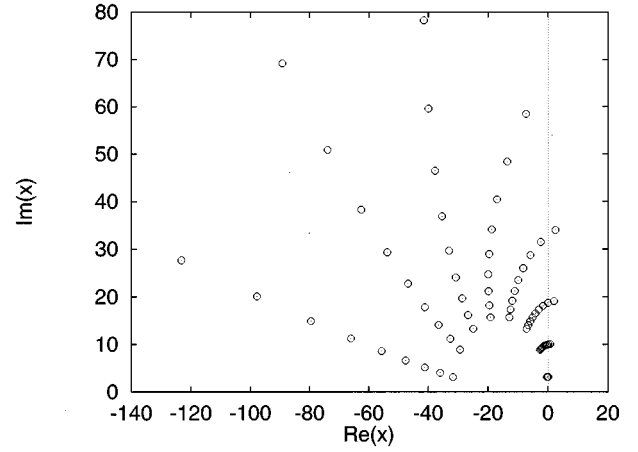


FIG. 1. Poles of the f_N^γ for $N=16$ and $N\gamma=0,2,4,\dots,16$. The poles are in concentric rings encircling $z = -16$; $N\gamma=0$ is the largest ring; $N\gamma=16$ is the smallest.

pared to f_F in Fig. 2. These occupation functions are very accurate for energies above about $x_{\text{bot}}(N, \gamma) = -4(2N - 12 + 6\gamma)/(1 + \gamma)^2$. At x_{bot} , f_N^γ has dropped by e^{-6} , about $\frac{1}{4}\%$. For $\gamma=1$ the function drops rapidly near $x_{\text{bot}}(N, \gamma)$. As γ is reduced the drop in the occupation function is less precipitous and occurs at lower energy. As a result the occupation functions employing smaller γ remain valid over a wider range. The fit to f_F near $x=0$ also improves. When $\gamma=0$ the second derivative agrees with that of f_F at $x=0$. The choice $\gamma=0$ therefore gives the best approximation for small $|x|$, but other choices yield better approximations over the whole range that is of interest in calculations.

Because values of γ smaller than 1 extend the range over which f_N^γ accurately reproduces f_F , smaller values of N can be used for a given bandwidth. The penalty for using smaller γ is that the maximum at positive energies grows and moves lower in energy. The low-energy tail of the occupation function also lengthens and may extend to core states. As mentioned in the introduction a different occupation function can be used for the single-site core states. The appropriate occupation for the single-site core states in this case is $f_{\text{core}} = 1 - f_N^\gamma$. The single-site core electron density and eigenvalues

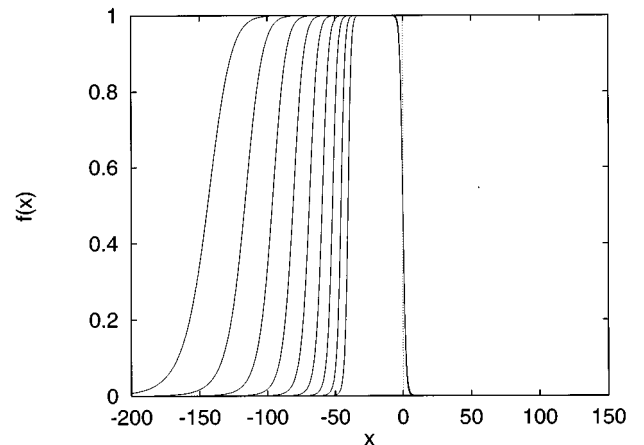


FIG. 2. The Fermi function is compared to f_N^γ for $N=16$ and $N\gamma=0,2,4,\dots,16$.

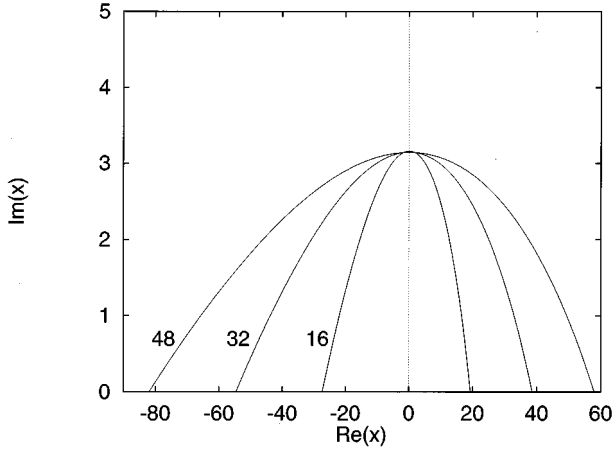


FIG. 3. The branch cut nearest μ is shown for $N=16, 32$, and 48 with $\gamma=3-\sqrt{8}$.

should be weighted by f_{core} , instead of one, since the other small contributions to the core density have already been included in the residues of f_N^γ . These residues account for the core banding for a fraction, $f_N^\gamma(\epsilon_{\text{core}})$, of each core level, ϵ_{core} . This is an advantage. It eliminates the need for an abrupt and arbitrary delineation between the valence band and core states.

In order to determine a “best” value for γ we considered the following. The function f_N^γ differs from f_F by an amount that can be expanded in powers of $1/N$:

$$f_F(x) - f_N^\gamma(x) = \frac{-x^2 e^x}{8N(1+e^x)^2} (1 - 6\gamma + \gamma^2) + O\left(\frac{1}{N^2}\right). \quad (15)$$

The value of γ that gives the most rapid convergence in N is $3-\sqrt{8}$ because it makes the $O(1/N)$ term vanish. This choice is independent of the band structure and eliminates the need or temptation to look for a value that optimizes a particular calculation. For this γ , the maximum at positive energies is located at $x=4.1N$ and has a value of 2.2^{-N} .

IV. ENTROPY

As alluded to in the introduction, evaluation of the entropy requires integrals involving logarithms of f_F as seen in Eq. (6). We take the branch cut of the logarithm to be along the negative real axis. This means that the entropy expression will have branch cuts where the phase of the approximation to e^z goes through odd multiples of π . These branch cuts emerge from $z=-2N/(1+\gamma)$, pass through the poles, and return to the real axis at $z=N/(1-\gamma)$. The branch cut nearest $\mu=0$ for $\gamma=3-\sqrt{8}$ is shown in Fig. 3 for the cases $N=16, 32$, and 48 . The integration required to evaluate the entropy cannot be reduced to a sum of residues because of the branch cuts. Fortunately the entropy is not required while the charge is iterated to self-consistency. It is needed only for the evaluation of the free energy. Furthermore the entropy integrand is zero except near μ , where it is sharply peaked. The most straightforward approach is to integrate along an arc that begins at $\mu-10K_B T$ and ends at $\mu+10K_B T$ spanning μ . However, such a contour would entail the evaluation

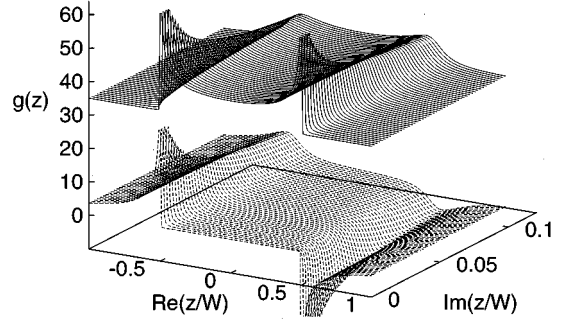


FIG. 4. The real and imaginary parts of $g(z)$ are shown in the upper half plane.

of the Green function at many points fairly close to the real axis. It is preferable to integrate along the branch cut closest to μ . This moves the integration away from the real axis to a region where the Green function is smoother and can usually be approximated by a ratio of linear functions of z . In many cases even a constant approximation is sufficient for energy differences. The coefficients of a rational fit can be determined from values at the pole (this would have already been calculated) and two additional points along the branch cut separated from the pole by $\approx 2k_B T$. The integration should actually be performed on a contour displaced slightly downward from the branch cut to avoid the singularity in the occupation function. It is computationally inexpensive to use as many points as are required to converge the integral because only the fit must be reevaluated. We find it convenient to integrate the singularity in the fit analytically.

V. EXAMPLE

Visual comparison of the approximate occupation functions to f_F satisfies us that they can be used interchangeably. However, our argument is that the stationarity of the free energy permits us to choose a very small value of N resulting in an occupation function, with only a few poles, that may significantly depart from f_F within the occupied band and yet the impact on the free energy remains small. To demonstrate this we calculate the free energy for a nearest-neighbor, single-band, tight-binding model for a one-dimensional chain for which the on-site Green function is

$$g(z) = -i \frac{20}{w} \frac{1}{\sqrt{1 - 4 \left(\frac{z - \epsilon_0}{w} \right)^2}}. \quad (16)$$

This $g(z)$ resembles (see Fig. 4) that of a transition metal; the band holds 10 electrons and has Van Hove singularities at the band edges. The band filling can be changed by adjusting ϵ_0 to move the band relative to μ , which is held fixed at zero. In Fig. 5 we show the error in the free energy that results from using $f_{N=16}^{\gamma=3-\sqrt{8}}$. This approximation works very well, and only fails at large bandwidths; it fails first at large band filling. This occurs simply because the width of the occupied band exceeds the range over which the approximation is valid, $|x_{\text{bot}}|$. This particular model $g(z)$ is very unforgiving in this regard because it has a singularity at the bot-

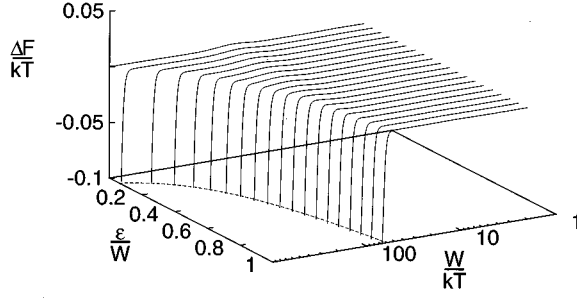


FIG. 5. Error in the free energy is shown for $N=16$ as a function of bandwidth and band filling. The curve in the base plane is $[x_{\text{bot}}/(\epsilon/w)]$, which is the width at which the occupation function deviates from one at the bottom of the band by about $\frac{1}{4}\%$.

tom of the band. Therefore, the effect from any deviation of the occupation function from the exact form at the bottom of the band is accentuated. However, in most real systems the density of states at the bottom of the band is free-electron like and goes smoothly to zero. Another feature in this plot is a low broad ridge that begins at $w \approx 60$ at zero band filling and moves to larger bandwidths as the filling increases. This small ridge results when the peak in f_N^γ at positive energies coincides with the top of the band. Even for $N=16$ this is a small error and we know from Eq. (12) that the height of the peak goes down exponentially with N . Increasing N to 32, we obtain essentially the exact free energy; see Fig. 6.

Alternatively it is always possible to increase the temperature and thereby move this smaller peak to a position above the “ d bands” where it will have a smaller effect. Going to higher temperatures also extends the validity of f_N^γ to lower energies, thus accommodating wider bands. However, it is usually the free energy at absolute zero, or room temperature, or at least somewhere below melting that is desired. The computational advantage of calculating at higher T must be weighed against the error of extending the high-temperature results to the temperature range of interest. The free energy at low temperature can often be accurately determined because we are doing more than extrapolation. We can calculate the free energy and entropy at a numerically convenient temperature and we know that the entropy at $T=0$ is zero. The negative of the entropy is the derivative of the free energy with respect to T ; so we can make a quadratic fit to the free energy. This implies that if $O(T^4)$ terms are small the energy at $T=0$ is given by the average of the free energy and the internal energy at any temperature, T_{calc} :¹⁰

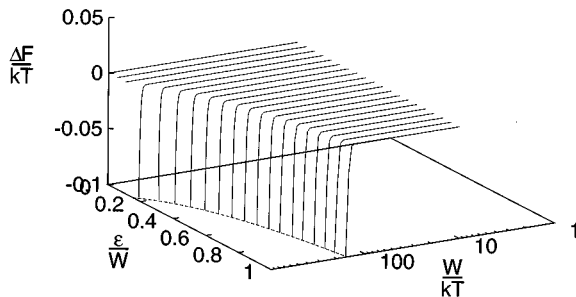


FIG. 6. Error in the free energy is shown for $N=32$ as a function of bandwidth and band filling.

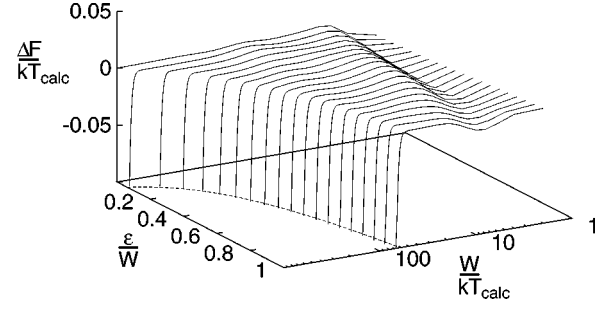


FIG. 7. Error in free energy at $T=0$ for $N=16$ as a function of bandwidth and band filling.

$$F(T=0) = \frac{F(T_{\text{calc}}) + [F(T_{\text{calc}}) + TS(T_{\text{calc}})]}{2}$$

$$= \frac{F(T_{\text{calc}}) + E(T_{\text{calc}})}{2}. \quad (17)$$

While the free energy is stationary with respect to the occupation function the internal energy and entropy are not. Hence there are errors, first order in the occupation function, that affect the $T=0$ free energy. We demonstrate that in practice these errors are small by calculating $[F(T_{\text{calc}}) + E(T_{\text{calc}})]/2$ with $f_{N=16}^{\gamma=3-\sqrt{8}}$ and f_F for our model system; in Fig. 7, we show the difference. The only region where differences are significant is for bands narrower than $\approx 10k_B T_{\text{calc}}$. For bands of typical width this corresponds to trying to find the $T=0$ energy from a calculation at a very high temperature. If we increase N to 32 the error at $T=0$ is reduced to essentially zero. We do not show a plot for this case because it is indistinguishable from Fig. 6.

The entropy used to construct Fig. 7 was evaluated with no approximation to $g(z)$. The entropy evaluated using a rational approximation to $g(z)$ as a function of bandwidth and filling is shown in Fig. 8. The entropy is reproduced accurately for bandwidths exceeding $\approx 10k_B T_{\text{calc}}$. Below this the width of the occupation function approaches that of the band and the rational approximation to $g(z)$ is not valid over the full integration range. A safe approach is to avoid temperatures above a tenth of the occupied bandwidth.

It can be seen in Eq. (6) that the entropy arises from only those energies where the occupation function departs from both 1 and 0. For f_F this happens only near μ , but for f_N^γ this also occurs far below μ where the occupation function drops

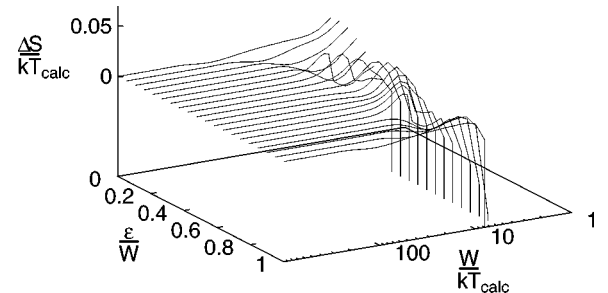


FIG. 8. The error in entropy that results from using a rational approximation to $g(z)$ is shown. The occupation function used is f_F .

slowly from 1 to 0. The temperature and N should be chosen so that at least the severest part of this drop is below the bottom of the band. In Figs. 5, 6, and 7, the “entropy” from the bottom of the band is included. This contribution is an artifact of the approximation and would not be present if f_F were used. When f_N^γ is used this entropy maintains the stationarity of the free energy. This entropy becomes non-negligible and therefore an issue only if N is chosen such that the bottom of the band is below the point $x_{\text{bot}}(N, \gamma)$, in the region where f_N^γ begins to drop below 1. This situation would occur only when maximum computational speed is being sought.

We have several options for dealing with the situation when $x_{\text{bot}}(N, \gamma)$ is above the bottom of the band. First, we could calculate the contribution to the eigenvalue sum that arises from the difference between f_N^γ and f_F and not include the entropy from the bottom of the band; this would entail calculations at additional energies and defeat the objective of greater speed. Second, we could calculate the density of states at a few points near the bottom of the band and evaluate the entropy based on either a constant, constant over linear, or linear over linear approximation to $g(z)$ near the pole of f_N^γ nearest the bottom of the band. This procedure is analogous to the evaluation of the entropy from the energy range near μ and costs essentially no time if the constant approximation is adopted. Third, we could simply ignore the first-order error introduced by failing to include the entropy

from the bottom of the band. This last and simplest option gives results that when plotted are indistinguishable from Fig. 7, which includes this entropy term. In light of this observation we propose that the entropy from the bottom of the band not be evaluated or evaluated with the constant approximation to $g(z)$.

VI. CONCLUSIONS

We have introduced a family of approximate occupation functions that accurately represent the Fermi occupation function over the range of typical bands. It is demonstrated for a model system that the free energy at finite temperature is given accurately and that a quadratic approximation to the temperature dependence gives accurate zero-temperature energies. The use of these functions can reduce the amount of computation required for each iteration in the solution of the Kohn-Sham equations. Furthermore, calculation at finite temperature often reduces the number of iterations required to reach convergence.

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