

things-to-do

Tigany Zarrouk

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1 Finite Electron Temperature

1. Gillian 1986 [?]

Finite electron temperature for estimation of the band energy at zero kelvin.

The finite-temperature scheme is merely a device, whose main purpose is to smooth discontinuities at the Fermi level.

Really want to get the ground state energy E_0 , for small T the free energy deviates from E_0 by a term quadratic in T : $A = E_0 - \frac{1}{2}\gamma T^2$ and that the deviation of the energy E is equal and opposite $E = E_0 + \frac{1}{2}\gamma T^2$. Therefore the best estimate for the ground-state energy will be $\frac{1}{2}(E + A)$ of which deviation from E_0 will only be $\mathcal{O}(T^3)$.

In the ground state the occupation numbers $f_{\mathbf{q}i}$ are equal to 1 for $\varepsilon_{\mathbf{q}i} < \mu$ and zero if $\varepsilon_{\mathbf{q}i} > \mu$, where $\varepsilon_{\mathbf{q}i}$ are Kohn-Sham eigenvalues at wavevector \mathbf{q} and μ is the chemical potential (Fermi Energy E_F).

In the case of a metal, this discontinuity of $f_{\mathbf{q}i}$ as a function of energy is troublesome. Because of occupation numbers, the response functions, (ASIDE: susceptibilities, linear response: think of polarisation $\mathbf{P} = \epsilon_0 \chi_e \mathbf{E}$, the measure of how polarisable a material is, or how well it *responds* to an electric field is χ)

$$\chi_2^0 \approx \frac{2}{\Omega} \sum_{\mathbf{q}} w_{\mathbf{q}} \sum_{G'} \frac{f_{\mathbf{q}}^0 + G' - f_{\mathbf{q}+G+G'}^0}{\varepsilon_{\mathbf{q}}^0 + G' - \varepsilon_{\mathbf{q}+G+G'}^0}$$

where $\varepsilon_{\mathbf{q}+G+G'}^0$ are non-interacting single-particle energies and $f_{\mathbf{k}}^0$ are the associated occupation numbers.

The point is that Brillouin zone sampling is effective with a small number of \mathbf{q} -vectors only if the function being sampled is smooth in *reciprocal* space. But because of the occupation numbers, the response function actually becomes far from smooth and is in fact discontinuous at zero temperature.

There is another related reason why we get trouble. Since we cannot know the self-consistent eigenvalues in advance, we do not know how many occupied states there will be at each \mathbf{q} . As the iteration progresses to self-consistency, eigenvalues at different \mathbf{q} will generally cross each other and the Fermi energy, and this would require a discontinuous change of occupation numbers. Such discontinuities would presumably play havoc with the minimisation scheme.

The solution we have adopted to these problems is to allow the $f_{\mathbf{q}i}$ to vary continuously in the range (0, 1). This has the effect both of smoothing the sampled function and of eliminating discontinuities due to level crossing. A convenient way of formulating this idea is to consider the calculation formally at finite temperature, and this is the reason for introducing the finite-temperature generalisation of density functional theory.

2. Horsfield 1996 [?]

Used Gillian's technique [?] with finite electron temperature for estimation of the band energy at zero kelvin.

Hamiltonian scales badly with system size $\mathcal{O}(N^3)$ for diagonalisation. Linear scaling works well for covalent materials as the density matrix is short ranged, but metals have had limited success other than with some moment's methods.

Short ranged density matrices can be made short ranged with a finite electron temperature, but leads to a weakening of the bonds, as electrons are promoted to higher energy states, making dynamic unrealistic.

For electronic degrees of freedom, one can work with the density matrix $\hat{\rho}$. The electron internal energy, $U(T)$, electron entropy $S(T)$ and the electron free energy $A(T)$ are

L^AT_EX

$$U(T) = 2\text{Tr}\{\hat{\rho}\hat{H}\} \quad (1)$$

$$S(T) = 2k_{\text{B}}\text{Tr}\{s(\hat{\rho})\} \quad (2)$$

$$A(T) = 2\text{Tr}\{\hat{\rho}\hat{H} - k_{\text{B}}Ts(\hat{\rho})\}, \quad (3)$$

where \hat{H} is the Hamiltonian and $s(\hat{\rho})$ is the entropy density.

L^AT_EX

$$\hat{\rho} = f(\hat{x}) = [1 + \exp(\hat{x})]^{-1} \quad (4)$$

$$s(f) = -[f\ln f + (1-f)\ln(1-f)] \quad (5)$$

where $\hat{x} = (\hat{H} - \mu)/k_{\text{B}}T$.

We can have an approximation to the free energy calculated exactly from the density matrix.

$$A(0) = U_0 \approx B(T) = A(T) + \frac{1}{2}TS(T)$$

Defining a more general functional we have

$$\Phi_{\alpha}(T) = A(T) + \alpha TS(T)$$

Taking the derivative of this with respect to position \mathbf{r}_i , for an atom i , we get the contribution to the force, at a constant number of electrons as

L^AT_EX

$$\Phi_{\alpha}(T) = 2\text{Tr}\{f(\hat{x})\hat{H} - (1-\alpha)k_{\text{B}}Ts(f(\hat{x}))\} \quad (6)$$

$$\mathbf{F}_i^{(\alpha)} = -2\text{Tr}\left\{\rho_{\text{eff}}^{(\alpha)}\frac{\partial\hat{H}}{\partial\mathbf{r}_i}\right\} \quad (7)$$

where

$$\langle\hat{x}\rangle = \frac{\text{Tr}\{\hat{x}f'(\hat{x})\}}{\text{Tr}\{f'(\hat{x})\}}$$

and

$$\rho_{\text{eff}}^{(\alpha)} = [f(\hat{x}) + \alpha(\hat{x} - \langle \hat{x} \rangle)f'(\hat{x})]$$

is an effective density matrix.

$\rho_{\text{eff}}^{(0.5)}$ appears to be an optimall approximation to the ground-state density matrix.

This works well if the electron temperature is less than 10% of the bandwidth.