Convergence of DFT eigenvalues with cell volume and vacuum level

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Computing work functions or absolute DFT eigenvalues (e.g. ionization potentials) requires some care. Obviously, we as discussing systems with surfaces in contact with vacuum — computing the absolute eigenvalue for the interior of an infinite crystal is not possible since the alignment with vacuum depends on the dipoles on the surface which are not being modeled. Therefore, what we really have in mind are 2D (slabs, sheets), 1D (polymers, nanotubes, nanowires) and 0D (molecules, atoms) where there are some periodic directions and some directions going into the vacuum. Let the lattice vector along the periodic direction be a and the lattice vector along the vacuum direction be L. We will be investigating the $L \to \infty$ limit below.

In general, the DFT Kohn-Sham Hamiltonian can be written as

$$H = -\frac{\nabla^2}{2m} + \phi(r) + V_{xc}(r)$$

where ϕ is the total electrostatic potential from all charges, ions and electrons,

$$\phi(r) = \int d^3r' \, \frac{\rho(r')}{|r - r'|} = \int \frac{d^3q}{(2\pi)^3} \frac{4\pi\tilde{\rho}(q)e^{iq\cdot r}}{q^2} \, .$$

Here, $\rho(r)$ is the total (ion+electron) charge density and $\tilde{\rho}(q)$ is its Fourier transform. Most of the problems with determining absolute energies and the vacuum level are because the Coulomb interaction is long ranged and so computing the potential in a periodic system of charges can be ill-defined. In could say it is about handling the $q = 0$ divergence in periodic systems.

Before continuing forward, there are two types of problems in determining absolute eigenvalues and potentials in a DFT calculation, and they are of different origin.

- First, *some* DFT codes will set the average potential to zero over the unit cell. This not only includes the electrostatic potential but also the exchange-correlation potential V_{xc}. This means that the average value of V_{xc} over the volume of the unit cell Ω,

  $$\frac{1}{\Omega} \int_\Omega d^3r \, V_{xc}(r) \, ,$$

  is being added or subtracted from the output potential. As the volume of the unit cell is changed by increasing or decreasing the vacuum, this average changes as well. Whether a

given code does this or not can only be determined by looking inside. If one is using a local or semi-local functional (e.g. LDA or GGA) and has enough vacuum for the electron density to be localized on the system, then the integral is just some number and the average will scale like $1/\Omega$. What this means is that the value of the potential in the vacuum region could have such a contribution that depends on Ω and must be corrected for or extrapolated away.

- Second, all DFT codes run on periodic systems will have to do something with the divergence at $q = 0$ and thus adjust the average potential in some way. This is what we are discussing below.

Before we begin, we will need some general orientation and one mathematical result. It has to do with the fact that for a function of compact support with well-defined Fourier transform, integrating over the Fourier space or summing over the discrete reciprocal (Fourier) lattice give *exactly* the same thing. We will do this in one dimension to keep the math simple. Consider two functions $F(x)$ and $G(x)$ whose product $F(g)G(x)$ is of compact support: it is non-zero only for $0 < x < a$. We want the integral of their product (inner product) which can be done in real or reciprocal space

$$I = \int_{-\infty}^{\infty} dx\, F(x)^* G(x) = \int_{-\infty}^{\infty} \frac{dq}{2\pi}\, \tilde{F}(q)^* \tilde{G}(q)$$

where the Fourier convention is

$$F(x) = \int_{-\infty}^{\infty} \frac{dq}{2\pi}\, \tilde{F}(q) e^{iqx}\,.$$

Instead of integrating over all x, let's take a unit cell of length $L > a$. Then the integral of $F(x)G(x)$ over the finite range $0 < x < L$ is also I. Once we are working on a finite interval of length L, we can make $F(x)$ and $G(x)$ periodic without changing I:

$$F_p(x) = \sum_{n=-\infty}^{\infty} F(x - nL) = \frac{1}{L} \sum_g \tilde{F}(g) e^{igx}$$

and similarly for $G_p(x)$. Here the reciprocal lattice vectors are $g = 2\pi n/L$ for integers n. I is unchanged if we use the periodic functions

$$I = \int_0^L dx\, F_p(x)^* G_p(x) = \frac{1}{L} \sum_g \tilde{F}(g)^* \tilde{G}(g)\,.$$

What we found is that

$$I = \int_{-\infty}^{\infty} \frac{dq}{2\pi}\, \tilde{F}(q)^* \tilde{G}(q) = \frac{1}{L} \sum_g \tilde{F}(g)^* \tilde{G}(g)\,.$$

The discrete sum and the continuous integral are *exactly* the same: for a function of compact support, one can sample discrete or continuously and no information is lost (Nyquist theorem).

We can write this in a slightly different way which is more useful below. We can choose to write $q = k + g$ where $-\pi/L < k < \pi/L$ is in the first Brillouin zone (BZ) and g a reciprocal lattice vector. Therefore

$$I = \sum_g \int_{-\pi/L}^{\pi/L} \frac{dk}{2\pi}\, \tilde{F}(k+g)^* \tilde{G}(k+g)\,.$$

Since the BZ has length $2\pi/L$ we change replace the integral by the average over the BZ and write

$$I = \frac{1}{L}\sum_g \left\langle \tilde{F}(k+g)^* \tilde{G}(k+g) \right\rangle_{BZ}$$

where

$$\langle h \rangle_{BZ} \equiv \int_{-\pi/L}^{\pi/L} \frac{dk}{2\pi/L}\, h(k)\,.$$

Thus another way to write out main finding is

$$I = \frac{1}{L}\sum_g \tilde{F}(g)^* \tilde{G}(g) = \frac{1}{L}\sum_g \left\langle \tilde{F}(k+g)^* \tilde{G}(k+g) \right\rangle_{BZ}.$$

Now we begin by focusing on the slab case. We have to periodic directions in the xy plane and one direction going into the vacuum. So if we let G_{xy} denote the reciprocal lattice vectors in the xy lattice, all functions of interest have periodicity in the xy plane and have a Fourier series in the xy plane: for example, the charge density $\rho(r)$ has Fourier representation

$$\rho(x,y,z) = \sum_{G_{xy}} \int_{-\infty}^{\infty} \frac{dq_z}{2\pi}\, \frac{\tilde{\rho}(G_{xy}, q_z)}{A} e^{iG_{xy}\cdot r_{xy} + iq_z z}\,.$$

The vector $r_{xy} = (x,y)$ is the position in the plane. A is the area of the periodic cell in xy.

Instead of looking at the potential $\phi(r)$ itself, consider the eigenvalue E_n for some bound stae $\psi_n(r)$:

$$E_n = \int d^3r\, \psi_n(r)^* \left[-\frac{\nabla^2}{2m} + \phi(r) + V_{xc}(r) \right] \psi_n(r)\,.$$

The part of interest is the electrostatic contribution

$$\Phi_n = \int d^3r\, \phi(r) |\psi_n(r)|^2\,.$$

To see this, let's define the Fourier transform of $|\psi_n(r)|^2$ to be $\tilde{p}_n(q)$. Then working in Fourier space

$$\Phi_n = \sum_{G_{xy}} \int \frac{dq_z}{2\pi} \frac{4\pi \tilde{\rho}(G_{xy}, q_z) \tilde{p}_n(G_{xy}, q_z)}{A(G_{xy}^2 + q_z^2)}\,.$$

Now, in an actual plane wave calculation, we have a periodic cell along z of length L. Both the bound state ψ_n and the charge density ρ will decay exponentially into the vacuum outside the slab. Thus for practical purposes, they have compact support. So by choosing a L large enough, the periodic images of these densities will not have any significant overlap so that the kinetic and exchange-correlation contributions to E_n will be very well converged for any reasonable L. It is again the electrostatic part that gives us trouble.

What the plane wave code actually calculates for Φ_n uses the discrete reciprocal lattice vectors G_z along z instead of a continuous q_z. The computed result from the periodic calculation is Φ_n^p and is

$$\Phi_n^p = \sum_{G_{xy}} \sum_{G_z} \frac{4\pi \tilde{\rho}(G_{xy}, G_z) \tilde{p}_n(G_{xy}, G_z)}{AL(G_{xy}^2 + G_z^2)} \qquad \text{where } G_{xy} = 0, G_z = 0 \text{ is excluded from the sum}\,.$$

(Most plane wave codes will write $\Omega = AL$ the cell volume instead of AL in the denominator.) We have to exclude the 0 wave vector contribution since the summand is very ill defined: the denominator goes to zero; while the numerator $\tilde{\rho}(q)$ also goes to zero for $q \to 0$ for a neutral system, it may only go to zero linearly for a system with a dipole moment so the result is poorly defined. This missing term and what to do with it is the basic problem.

Using our mathematical result, for any $G_{xy} \neq 0$, all the integrands or summands are quite smooth so we can use the equivalence of the continuous integral and discrete sum along z to find

$$\int_{-\infty}^{\infty} \frac{dq_z}{2\pi} \frac{4\pi\tilde{\rho}(G_{xy}, q_z)\tilde{p}_n(G_{xy}, q_z)}{A(G_{xy}^2 + q_z^2)} = \sum_{G_z} \frac{4\pi\tilde{\rho}(G_{xy}, G_z)\tilde{p}_n(G_{xy}, G_z)}{AL(G_{xy}^2 + G_z^2)} \,.$$

However, for $G_{xy} = 0$, we can't just blindly apply the mathematical equivalence since the integrand is actually divergent for $G_z = 0$ while the integral is generally well defined for physical systems (see below).

Thus far, we have shown that all $G_{xy} \neq 0$ terms are identical between Φ_n and Φ_n^p so that

$$\Phi_n = \Phi_n^p + \int_{-\infty}^{\infty} \frac{dq_z}{2\pi} \frac{4\pi\tilde{\rho}(q_z)\tilde{p}_n(q_z)}{Aq_z^2} - \sum_{G_z \neq 0} \frac{4\pi\tilde{\rho}(G_z)\tilde{p}_n(G_z)}{ALG_z^2} \,.$$

To clarify the difference further, we can write an arbitrary q_z as the sum of the closest G_z plus some k_z that is in the first BZ $q_z = k_z + G_z$ as we did in our mathematical result above. We then have the equivalent expression

$$\Phi_n = \Phi_n^p + \frac{4\pi}{AL}\Big\langle \frac{\tilde{\rho}(k_z)\tilde{p}_n(k_z)}{k_z^2} \Big\rangle_{BZ} + \frac{4\pi}{AL} \sum_{G_z \neq 0} \left[\Big\langle \frac{\tilde{\rho}(k_z + G_z)\tilde{p}_n(k_z + G_z)}{(k_z + G_z)^2} \Big\rangle_{BZ} - \frac{\tilde{\rho}(G_z)\tilde{p}_n(G_z)}{G_z^2} \right] .$$

To proceed, we need to look at some of the physical characteristics of $\tilde{\rho}$ and $\tilde{p}_n$. We expand both in series

$$\tilde{\rho}(k) = \alpha k + \beta k^2 + O(k^3) \quad , \quad \tilde{p}_n(k) = 1 + \alpha_n k + \beta_n k^2 + O(k^3) \,.$$

The expansion for $\tilde{\rho}$ starts at dipolar order because our system is net neutral. The p_n expansion starts at 1 since $|\psi_n(r)|^2$ is normalized. The product will behave like

$$\tilde{\rho}(k)\tilde{p}_n(k) = \alpha k + Qk^2 + O(k^3) + O(k^4) + \cdots$$

This product divided by k^2 is then

$$\frac{\tilde{\rho}(k)\tilde{p}_n(k)}{k^2} = \frac{\alpha}{k} + Q + O(k) + O(k^2) + \cdots$$

This looks badly divergent, but the reciprocal lattice vectors and the BZ have inversion symmetry: for any valid G_z, $-G_z$ is also valid and for any k_z in the BZ, so is $-k_z$. Thus the BZ average as well as the sum over G_z in the expression for Φ_n are both sampling the divergent α/k term equally along positive and negative values so its contribution actually vanishes around the origin. Thus the effective summands are actually quite smooth here.

What this means is that the sum over $G_z \neq 0$ terms above is very small since we are subtracting the average of a smooth function over the BZ from the value at the center of the BZ; anyways, the

difference converges to zero as L gets larger and the averaging is over a narrower region. Therefore, any type of discrepancy between Φ_n and Φ_p is really coming from the very first term:

$$\Phi_n = \Phi_n^p + \frac{4\pi}{AL}\Big\langle \frac{\tilde{\rho}(k_z)\tilde{p}_n(k_z)}{k_z^2}\Big\rangle_{BZ} + \text{terms converging very rapidly in } L\,.$$

Using the Taylor series in k from above, the desired average is

$$\frac{4\pi}{AL}\Big\langle \frac{\tilde{\rho}(k_z)\tilde{p}_n(k_z)}{k_z^2}\Big\rangle_{BZ} = \frac{4\pi}{AL}\Big\langle \frac{\alpha}{k} + Q + Rk + Sk^2 + \cdots \Big\rangle_{BZ}\,.$$

Only the even terms survive, and the average of k^2 is proportional to $(\pi/L)^2$. So we get

$$\frac{4\pi}{AL}\Big\langle \frac{\tilde{\rho}(k_z)\tilde{p}_n(k_z)}{k_z^2}\Big\rangle_{BZ} = \frac{C}{L} + \frac{D}{L^3} + \frac{E}{L^5} + \cdots$$

for some constants in the numerators. Therefore, we expect for the eigenvalue

$$E_n(L) = E_n(\infty) + CL^{-1} + DL^{-3} + \cdots$$

By performing a set of computations at various L, we can fit $E_n(L)$ to the above form and extrapolate to $L = \infty$ to get $E_n(\infty)$. (This is an example of Richardson extrapolation.) This concludes the slab geometry.

Considering the other geometries (1D wire and 0D molecule) is mainly taking the above derivation and changing some discrete sums to continuous ones. For example, for a wire geometry with periodic axis along z, the x and y directions are those going into the vacuum. Thus we will have a discrete sum over G_z and integrals over q_x and q_y; when we put in a periodic box we get a discretized sum over G_x and G_y instead; the volume factor AL is replaced by aL^2 where a is the periodic lattice length along z; the $G_z \neq 0$ contributions will be well behaved while $G_z = 0$ will be problematic; for $G_z = 0$, the contributions for $(G_x, G_y) \neq 0$ and those from averaging over a BZ centered around (G_x, G_y) will be very close; so the difference between Φ_n and Φ_n^p will again be due to the averaging in the BZ around $q = 0$. The main difference is that now we have vector k so

$$\tilde{\rho}(k)\tilde{p}_n(k) = \alpha^T k + k^T Q k + O(k^3)$$

where α is a vector, Q is a matrix, etc., and

$$\frac{\tilde{\rho}(k)\tilde{p}_n(k)}{k^2} = \frac{\alpha^T \hat{k}}{k} + \hat{k}^T Q \hat{k} + O(\hat{k}\hat{k}k) + O(\hat{k}\hat{k}kk) + \cdots$$

where $\hat{k} = k/|k|$ is the unit vector. The averaging proceeds as before noting that the odd power cancel by symmetry and the even terms give for the average of k^2 something of order $(\pi/L)^2$. The overall volume prefactor is now $1/(aL^2)$ so our expansion will look like

$$E_n(L) = E_n(\infty) + CL^{-2} + DL^{-4} + \cdots$$

The 0D point geometry has vacuum in all directions so the q integrals are continuous along all three directions; the discretization is to replace q by a three vector G; the volume factor is $\Omega = L^3$; and we proceed as before. So the series starts with L^{-3} and goes in powers of two from there.

Our final summary is thus that

$$E_n(L) - E_n(\infty) = \frac{\text{constant}}{\Omega} + \text{subleading terms} = \begin{cases} CL^{-1} + DL^{-3} + \cdots & \text{2D slab case} \\ EL^{-2} + FL^{-4} + \cdots & \text{1D wire case} \\ GL^{-3} + HL^{-5} + \cdots & \text{0D point case} \end{cases} .$$

for constants $C, D, \ldots$ Therefore, we expect the eigenvalue to converge to the $L \to \infty$ limit as

$$E_n(L) = E_n(\infty) + \frac{C}{L^m} + \frac{D}{L^{m+2}} + \cdots$$

where $m = 1$ for 2D, $m = 2$ for 1D, and $m = 3$ for 0D. By performing a set of computations at various L, we can fit $E_n(L)$ to the above form and extrapolate to $L = \infty$ to get $E_n(\infty)$. (This is an example of Richardson extrapolation.)