Impurity problem, relation to doping, densities of state

Sohrab Ismail-Beigi

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The basic motivation is to see what happens when we have a dopant/impurity in a metallic system where the Fermi level cuts through a band. Does the dopant in fact raise the Fermi level? By how much and in what circumstances? The question comes up when creating oxygen vacancies in a metallic oxide, for example an oxygen vacancy in $\mathrm{LaNiO_3}$. Clearly, there is a perturbation to the electronic structure around the vacancy site and oxygen vacancies should donate electrons since the oxygen p bands are below the Fermi level. But do they? What if a bound state forms?

More generally, even in a semiconductor, does the raising of the Fermi level correspond exactly to the number of electrons being donated? Or does the change in the density of states around the vacancy modify the counting even if a bound state does not form?

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1 Warmup: Dirac delta potential in one dimension

While not really quite what we want to look at, (i) since in one dimension any type of attractive potential gives a bound state and (ii) we have a discrete lattice problem and not a continuum one, this gives us some basic ideas of what happens to the local density of states as a function of energy and position. Also it illustrates some basic facts in the simplest possible manner and in a direct manner.

The Hamiltonian is

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - V\delta(x)$$

where V can have either sign. For an eigenstate ψ_E of energy E where $H\psi_E = E\psi_E$, integrating around the origin gives $-V\psi_E(0) = (\hbar^2/2m)[\psi'_E(0^+) - \psi'_E(0^-)$.

When $V > 0$ we get a bound state $\psi_E(x) = \sqrt{\kappa}\exp(-\kappa|x|)$ with $\kappa = mV/\hbar^2$ and $E = -E_b = -mV^2/(2\hbar^2)$. For $V < 0$ we have a repulsive potential and obviously no bound states.

For the scattering states $E \geq 0$, we look for real wave functions to exploit the symmetry of the potential: since we get free electron states for $x \neq 0$, the wave functions are sines or cosines. We write $E = \hbar^2 k^2/(2m)$. One eigenfunction is odd and is $\psi_E(x) = \sin(kx)$ which is a solution since it is continuous around origin and has zero value at origin. The even case must look like $\psi_E(x) = \cos(k|x| + \phi)$. Applying the condition around the origin gives $\tan\phi = mV/(k\hbar^2) = \sqrt{E_b/E}$. Some minor algebra then gives $\cos\phi = \sqrt{E/(E+E_b)}$ and $\sin\phi = \sqrt{E_b/(E+E_b)}$. Notice the bound state energy E_b enters this form and sets the energy scale even if we have the repulsive case $V < 0$.

The local density of states at energy E and position x for $E \geq 0$ is (proportional to)

$$D(E,x) = \sum_E |\psi_E(x)|^2 = \cos(k|x| + \phi)^2 + \sin(kx)^2\,.$$

Some trigonometry and substitution then gives a few equivalent forms

$$\begin{aligned}
D(E,x) &= 1 - (\sin\phi)\Big[\cos(2k|x|)\sin\phi + \sin(2k|x|)\cos\phi\Big] \\
&= 1 - \sin\phi\sin(2k|x| + \phi) \\
&= 1 - \sqrt{\frac{E_b}{E+E_b}}\sin\left(2k|x| + \tan^{-1}(\sqrt{E_b/E})\right) \\
&= 1 - \frac{E_b\cos(2k|x|) + \sqrt{EE_b}\sin(2k|x|)}{E+E_b}\,.
\end{aligned}$$

At the origin, we have

$$D(E,0) = \frac{E}{E+E_b}$$

which clearly shows a reduction in the density of states for low energy $E < E_b$. The more general formula has been written as the unperturbed results "1" minus a correction

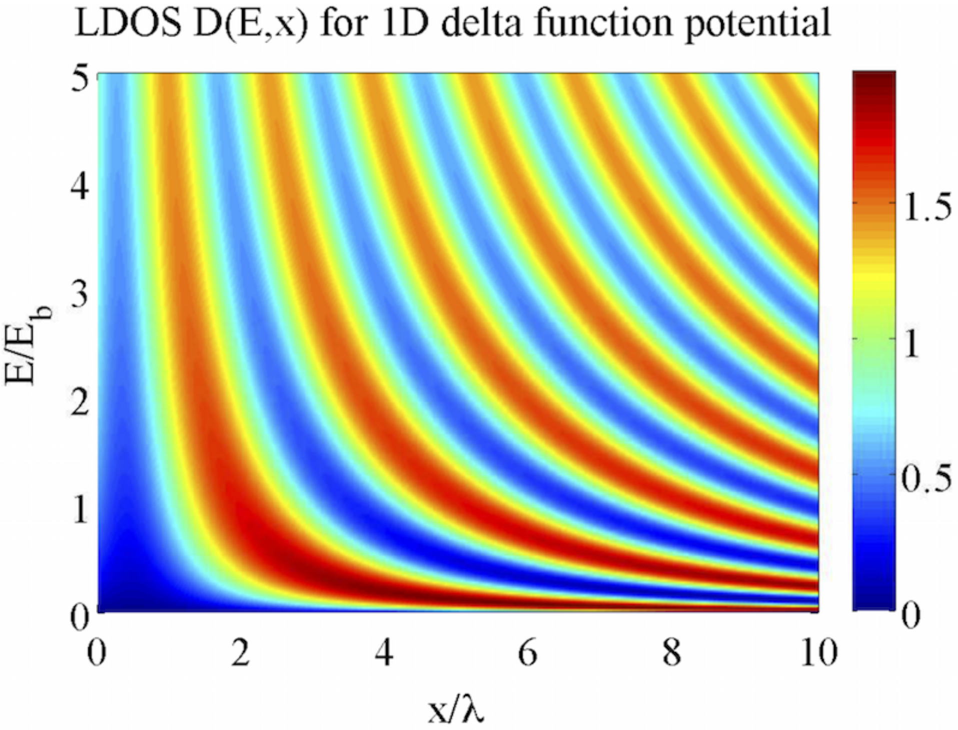

Figure 1: The local density of states $D(E,x)$ for the one dimensional delta function potential in scaled units. The suppression at small x and small energies E is quite apparent, as is the oscillatory nature of the function versus x.

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which represents this suppression/enhancement. The correction is oscillatory in x with wavelength half that of the wavelength for that energy. For any x, once $E \ll E_b$, we get $D(x,E) \to 1-\cos(2k|x|)$ which reduces the weight around the origin and moves it elsewhere in an oscillatory manner. For high energies $E \gg E_b$, we get a small wiggly correction $D(x,E) \to 1-\sqrt{E_b/E}\sin(2k|x|)$. A more precise way to attack this is to rescale the energy and distance: we measure energies with respect to E_b and distances with respect to $\lambda = \hbar^2/(m|V|)$ which is the bound state size (exponential decay length). We get

$$D(E,x) = 1 - \frac{\cos\left(2\cdot\sqrt{E/E_b}\cdot|x|/\lambda\right) + \sqrt{E/E_b}\cdot\sin\left(2\cdot\sqrt{E/E_b}\cdot|x|/\lambda\right)}{1+E/E_b}.$$

Figure 1 shows a plot of this local density of states. We note the reduction in density of states for small positions x and small energies: either the bound state has formed and by orthogonality other states “stay away” or the potential is repulsive and they get “pushed away”. The potential has changed the density of quantum states in an interesting way.

In fact, one can see there are four overall regions in the figure. They are: (i) small energy and small distance from origin: $E/E_b, |x|/\lambda \ll 1$ and the LDOS is just depressed strongly to close to zero; (ii) small energy and far from origin: $E/E_b \ll 1 \ll |x|/\lambda$ where the LDOS is only suppressed for the smallest of energies but then has a rapid growth with energy reaching a sharp peak above 1 before falling and oscillating with decaying amplitude; (iii) higher energy but close to origin: $|x|/\lambda \ll 1 \ll E/E_b$ where the LDOS is suppressed but gradually recovers to unity as energy increases; (iv) high energy and far away $E/E_b, |x|/\lambda \gg 1$ where the LDOS oscillates around one in a "regular" manner.

Finally, the last thing to note is a general sum rule of "conservation" rule for the number of quantum states at each position: namely it is unchanged by any perturbation. What we mean is that

$$\int D(x,E)dE = \text{fixed number}\,.$$

While hard to see this from the formula above, one just appeals to the basic definition of the local density of states:

$$D(x,E) = \sum_{E'} |\psi_{E'}(x)|^2 \delta(E-E')$$

so that

$$\int D(x,E)dE = \sum_{E'} |\psi_{E'}(x)|^2 = \langle x|x\rangle$$

which is a fixed number (infinite for a true 1D continuum but finite for a discrete lattice system or a system with a cutoff). This is an important fact to keep in mind: a perturbation can rearrange the local density of states at x in a significant way as a function of energy E, but the total number of states at x remain unchanged.

2 Lattice with localized impurity: densities of states

Consider some unperturbed periodic lattice system with N sites labeled by α or β at lattice positions r_α. We will assume a single orbital per site for mathematical convenience but some of the results below are more general. It's Green's function is

$$G^0_{\alpha\beta}(\omega) = \frac{1}{N}\sum_k \frac{e^{ik\cdot(r_\alpha - r_\beta)}}{\omega - \epsilon_k + i0^+}$$

We take the on-site energy to be zero so the average value of ϵ_k is zero and $\omega = 0$ will be the center of the band. Here, ϵ_k is the dispersion relation.

We will be perturbing this system by introducing a well of depth V at site zero. So our perturbation operator $H'_{\alpha\beta} = -V\delta_{\alpha,0}\delta_{\beta,0}$. The Dyson equation and T matrix are defined via

$$G = G^0 + G^0 H' G = G^0 + G^0 T G^0$$

Repeated iteration of the Dyson equation gives

$$G_{\alpha\beta} = G^0_{\alpha\beta} - G^0_{\alpha 0} V G^0_{0\beta} + G^0_{\alpha 0} V G^0_{00} V G^0_{0\beta} + \cdots$$

which sums to

$$T_{\alpha\beta} = \delta_{\alpha,0}\delta_{\beta,0}T_{00} = \delta_{\alpha,0}\delta_{\beta,0} \cdot \frac{-V}{1+gV}$$

where we have defined the unperturbed on-site Green's function $g(\omega)$ via

$$g(\omega) \equiv G^0_{00} = G^0_{\alpha\alpha} = \frac{1}{N}\sum_k \frac{1}{\omega - \epsilon_k + i0^+} = \int \frac{D^0(E)}{\omega - E + i0^+}dE$$

where $D^0(\omega)$ is the density of states per site for the unperturbed system. We can then write the Green's function as

$$G_{\alpha\beta}(\omega) = G^0_{\alpha\beta}(\omega) - \frac{G^0_{\alpha,0}(\omega)G^0_{0,\beta}(\omega)V}{1+g(\omega)V}$$

We will also define the off-site unperturbed Green's function $g(\omega, r_\alpha)$ via

$$g(\omega, r_\alpha) \equiv \frac{1}{N}\sum_k \frac{e^{ik\cdot r_\alpha}}{\omega - \epsilon_k + i0^+} = \frac{1}{N}\sum_k \frac{\cos(k\cdot r_\alpha)}{\omega - \epsilon_k + i0^+}$$

where we have used time-reversal $\epsilon_k = \epsilon_{-k}$. This also means $g(\omega, r_\alpha) = g(\omega, -r_\alpha)$. So we can write

$$G_{\alpha\beta}(\omega) = G^0_{\alpha\beta}(\omega) - \frac{g(\omega, r_\alpha)g(\omega, r_\beta)V}{1+g(\omega)V}$$

The local density of states is given by the usual relation

$$D(\omega, \alpha) = -\frac{1}{\pi}Im\; G_{\alpha\alpha}(\omega)\,.$$

The LDOS at the impurity site $\alpha = 0$ is particularly simple

$$D(\omega, 0) = D^0(\omega) + \frac{1}{\pi}Im\frac{g(\omega)^2V}{1+g(\omega)V} = -\frac{1}{\pi}Im\;\frac{g(\omega)}{1+g(\omega)V}$$

while the LDOS at other sites is

$$D(\omega, \alpha) = D^0(\omega) + \frac{1}{\pi}Im\left[\frac{g(\omega, r_\alpha)^2V}{1+g(\omega)V}\right]\,.$$

To make some useful definitions for what follows, we define the real and imaginary parts of $g(\omega)$ as follows

$$g(\omega) = R(\omega) - i\pi D^0(\omega)\,.$$

The two are not independent of course since we have, for example,

$$R(\omega) = P\int \frac{D^0(E)}{\omega - E}dE = \lim_{\epsilon\to 0^+}\left(\int^{\omega-\epsilon} + \int_{\omega+\epsilon}\right)\frac{D^0(E)}{\omega - E}dE\,.$$

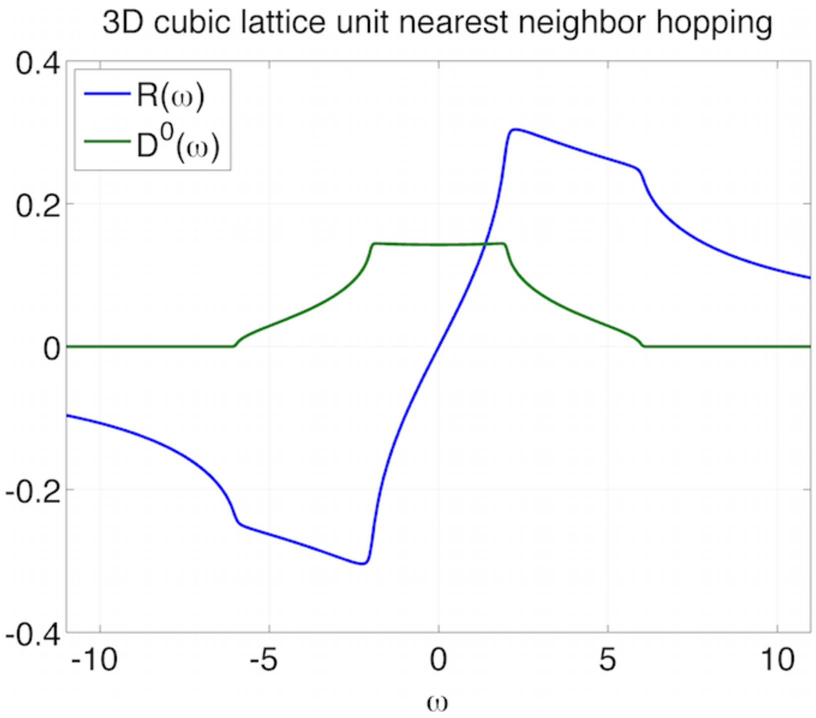


Figure 2: $R(\omega)$ and $D^0(\omega)$ for the 3D cubic lattice with one orbital per site, nearest neighbor hopping of -1 and zero on site energy. The maximum magnitude of R is ≈ 0.304 and happens inside the energy band. It's magnitude at the band edge $\omega = \pm 6$ is ≈ 0.239.

These two are plotted in Figure 2 for a cubic lattice with nearest neighbor hopping $t = -1$ in three dimensions so the band is centered around $\omega = 0$ and extends from -6 to 6 in energy. Van Hove singularities are clearly visible in the density of states as well.

To see if a genuine bound state forms outside the band, we can look at the LDOS at the impurity site which can be arranged to be

$$D(\omega, 0) = \frac{D^0(\omega)}{(1 + R(\omega)V)^2 + (\pi V D^0(\omega))^2} .$$

Outside the band, D^0 is infinitesimally small so we get a bound state when $R(\omega)V = 1$. Since R decreases in magnitude starting at the band edge and going away from it, there will be a minimum V needed to get a bound state which is $1/R$ at the band edge or approximately $V = 4.18$ from Figure 2. But regardless, we see that the density of states is modified inside the band as well no matter whether the bound state is formed or not. In the limit of weak V, we get

$$D(\omega, 0) = D^0(\omega) \cdot \left[1 - 2R(\omega)V + O(V^2)\right]$$

which enhances the LDOS at low energies (where $R < 0$) and suppresses at high energies. In the limit of very large V, other than the bound state outside the band, $D \sim 1/V^2$ inside the band which goes to zero: the bound state "eats up" all the density of states and the impurity site has no weight for the rest of the energies. This just mean the impurity bound state is extremely localized and has "decoupled" from the rest of the lattice.

For the other sites, $D(\omega, \alpha)$ is the original unperturbed DOS plus a correction which has $g(\omega, r_\alpha)^2$. The Green's function $g(\omega, r_\alpha)$ generally will decay with r_α getting larger: this is easy to see from its definition

$$g(\omega, r_\alpha) = \frac{1}{N} \sum_k \frac{\cos(k \cdot r_\alpha)}{\omega - \epsilon_k + i0^+}$$

where compared to $r_\alpha = 0$, the cosine factor will cause cancellations. For example, for ω outside the band, the integrand over k is smooth and is in fact a Fourier transform of a periodic function so it will decay exponentially with $|r_\alpha|$. Inside the band, the suppression is not so strong but still exists: for example, the imaginary part corresponding to a density of states is

$$-\frac{1}{\pi} Im\ g(\omega, r_\alpha) = \frac{1}{N} \sum_k \cos(k \cdot r_\alpha) \delta(\omega - \epsilon_k) = D^0(\omega) \langle \cos(k \cdot r_\alpha) \rangle |_{\omega = e_k}$$

where we average over the surface in k space $\omega = \epsilon_k$.

Figure 3 shows local densities of states at the impurity site and around it for a variety of well depths V. The plots contain a good deal of information, but some simple observations are: (i) the recover to the unperturbed DOS as we move away from the impurity is quite rapid for any V; (ii) the LDOS at the impurity site is always enhanced at low energies and suppressed at high energies; (iii) the LDOS of the next closest site (1,0,0) is more complex: (iii.a) for weaker V without a bound state, it is enhanced for the lowest energies but then is suppressed at slightly higher energies, (iii.b) for bigger V where the bound state just starts developing, it has significant amplitude at the bound state energy and generally a suppressed weight at lower energies in the band, (iii.c) for very strong V its weight on the impurity bound state drops (since the impurity bound state is getting quite localized on the origin) but the main thing we see is a band narrowing where its LDOS is suppressed at higher and lower energies but is enhanced in the center of the band: this reflects the fact that as the bound state becomes very deep, it effectively decouples from the system so that site (1,0,0) now has no hopping allowed in one direction and effective has less hopping or is in a lower dimension subsystem to its "has a narrower band" thinking intuitively. Or more precisely, the energy of the site is better defined (since it has less hoppings off of it) and thus its weight in the spectrum of states is narrower in energy.

3 Density of state modification and doping

If we are interested in the doping aspect, i.e. the impurity is for example a vacancy site that donates electrons to the system, we will need to deal with the total density of states and the

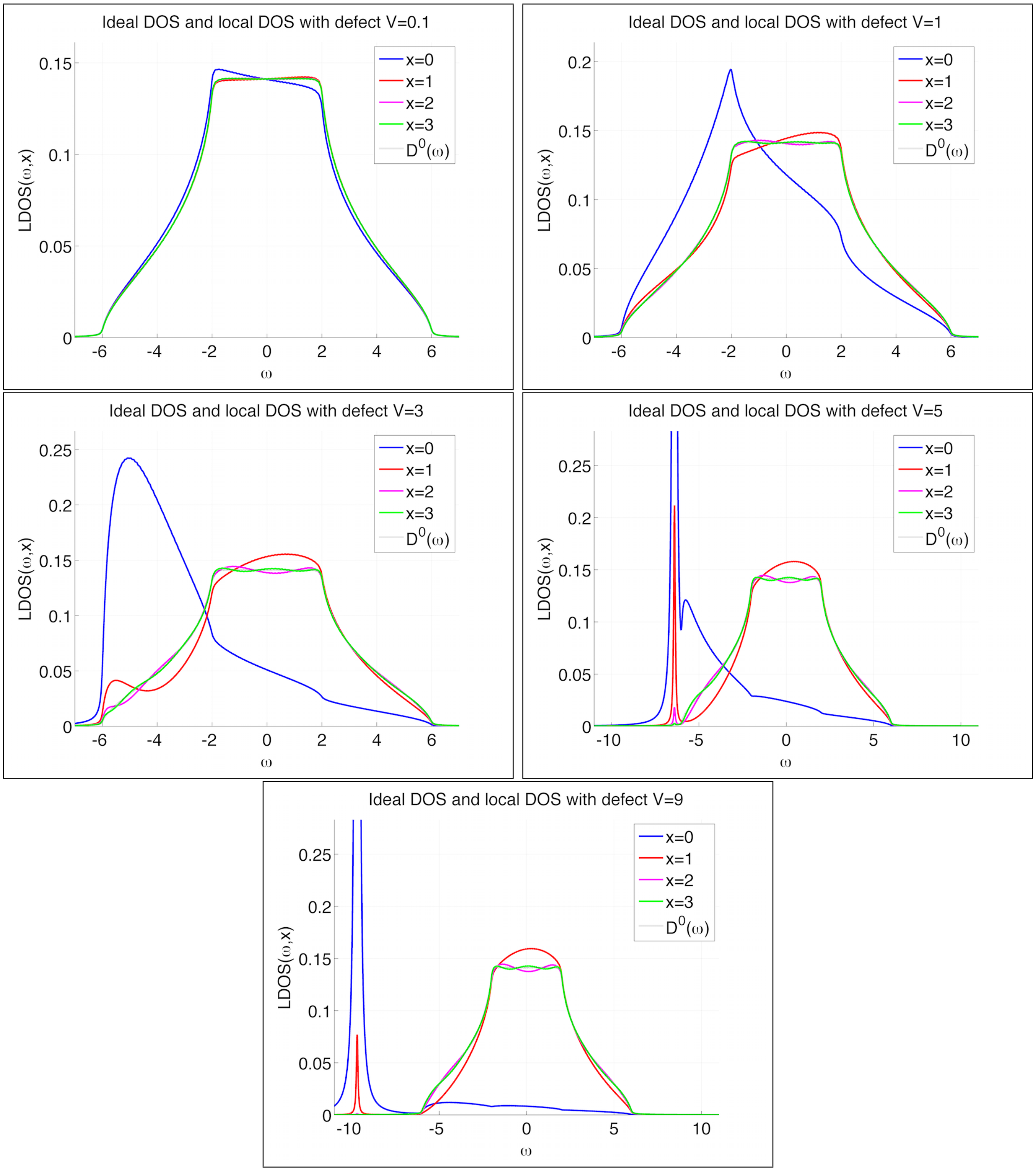


Figure 3: Local densities of states at sites $(x, 0, 0)$ as a function of impurity well-depth V for the simple 3D cubic lattice with nearest neighbor hoppings. The ideal lattice density of states per site is also shown for comparison. In general, the change in the local density of states is quite localized for the range of V.

Fermi level. The total density of states is

$$D_{tot}(\omega) = \sum_\alpha D(\omega,\alpha) = ND^0(\omega) + \frac{1}{\pi} Im\left[\frac{V}{1+g(\omega)V}\sum_\alpha g(\omega,r_\alpha)^2\right] .$$

The sum in question is

$$\sum_\alpha g(\omega,r_\alpha)^2 = \sum_\alpha \frac{1}{N}\sum_k \frac{e^{ik\cdot r_\alpha}}{\omega-\epsilon_k+i0^+}\frac{1}{N}\sum_{k'}\frac{e^{ik'\cdot r_\alpha}}{\omega-\epsilon_{k'}+i0^+} = \frac{1}{N}\sum_k \frac{1}{(\omega-\epsilon_k+i0^+)^2} .$$

The interesting thing is that this is given by a derivative of a know quantity

$$\sum_\alpha g(\omega,r_\alpha)^2 = -\frac{\partial}{\partial\omega}\frac{1}{N}\sum_k \frac{1}{(\omega-\epsilon_k+i0^+)} = -\frac{dg(\omega)}{d\omega} .$$

So

$$\begin{aligned} D_{tot}(\omega) &= \sum_\alpha D(\omega,\alpha) = ND^0(\omega) - \frac{1}{\pi} Im\left[\frac{g'(\omega)V}{1+g(\omega)V}\right] \\ &= ND^0(\omega) - \frac{d}{d\omega}\left(\frac{1}{\pi} Im \ln\Big[1+g(\omega)V\Big]\right) . \end{aligned}$$

This is in a very nice and practical form since we can write

$$D_{tot}(\omega) = ND^0(\omega) + \Delta D_{tot}(\omega)$$

which isolates the change in the total density of states due to the impurity and we now have an explicit expression for $\Delta D_{tot}(\omega)$. Specifically, let us say our ideal lattice of N sites had M_0 electrons which then determined the unperturbed chemical potential μ_0 via

$$M_0 = N\int^{\mu_0} D^0(E)dE .$$

The creation of the impurity will change the number of electrons to $M = M_0 + \delta$. The new chemical potential is set by

$$M = \int^{\mu} D_{tot}(E)dE .$$

At this point we will make some simple assumptions: the lattice is thermodynamically large so that we will work to leading order in $1/N$ to find the change of chemical potential because $\Delta D_{tot} = O(1)$ as well which is clearly what we found analytically above. Letting $\mu = \mu_0 + \Delta\mu$ where $\Delta\mu = O(1/N)$ then gives, after some minor algebra, to $O(1/N)$,

$$\delta = \Delta\mu \cdot ND^0(\mu_0) + \int^{\mu_0} \Delta D_{tot}(E)dE$$

which says the added electrons raise the Fermi level according to the (large) unperturbed DOS but are also accommodated by the change of DOS due to the introduction of the impurity. The change of chemical potential is

$$\Delta\mu = \frac{\delta - \int^{\mu_0}\Delta D_{tot}(E)dE}{ND^0(\mu_0)} .$$

So in fact the chemical potential never rises as much as we would expect from the unperturbed density of states. If the DOS is suppressed at lower energies, it rises further; if the DOS is enhanced at low energies, it rises less. If an impurity bound state appears below the lower band edge, then the integral over it will give an integer which could accommodate all (or some) of the doped electrons δ.

Figure 4 shows the unperturbed density of states as well as the change of total density of states as well as their cumulative integrals. Once the potential depth is significant, the change of total DOS can accommodate a significant fraction of an electron at low energies (definitely an entire electron by the time the bound state is well developed) even if no bound state has formed yet as in the $V = 3$ case.

Using the actual formula for the change of density of states, we get

$$\begin{aligned}\int^{\mu_0} \Delta D_{tot}(E)dE &= -\frac{1}{\pi}\arg(1+g(\mu_0)V) = \frac{1}{\pi}\arg\Big(1+R(\mu_0)V+i\pi V D^0(\mu_0)\Big) \\ &= \frac{1}{\pi}\cos^{-1}\left(\frac{1+R(\mu_0)V}{\sqrt{(1+R(\mu_0)V)^2+(\pi V D^0(\mu_0))^2}}\right)\end{aligned}$$

In the limit of weak V, we can series expand to get

$$\int^{\mu_0} \Delta D_{tot}(E)dE = V D^0(\mu_0) + O(V^2)$$

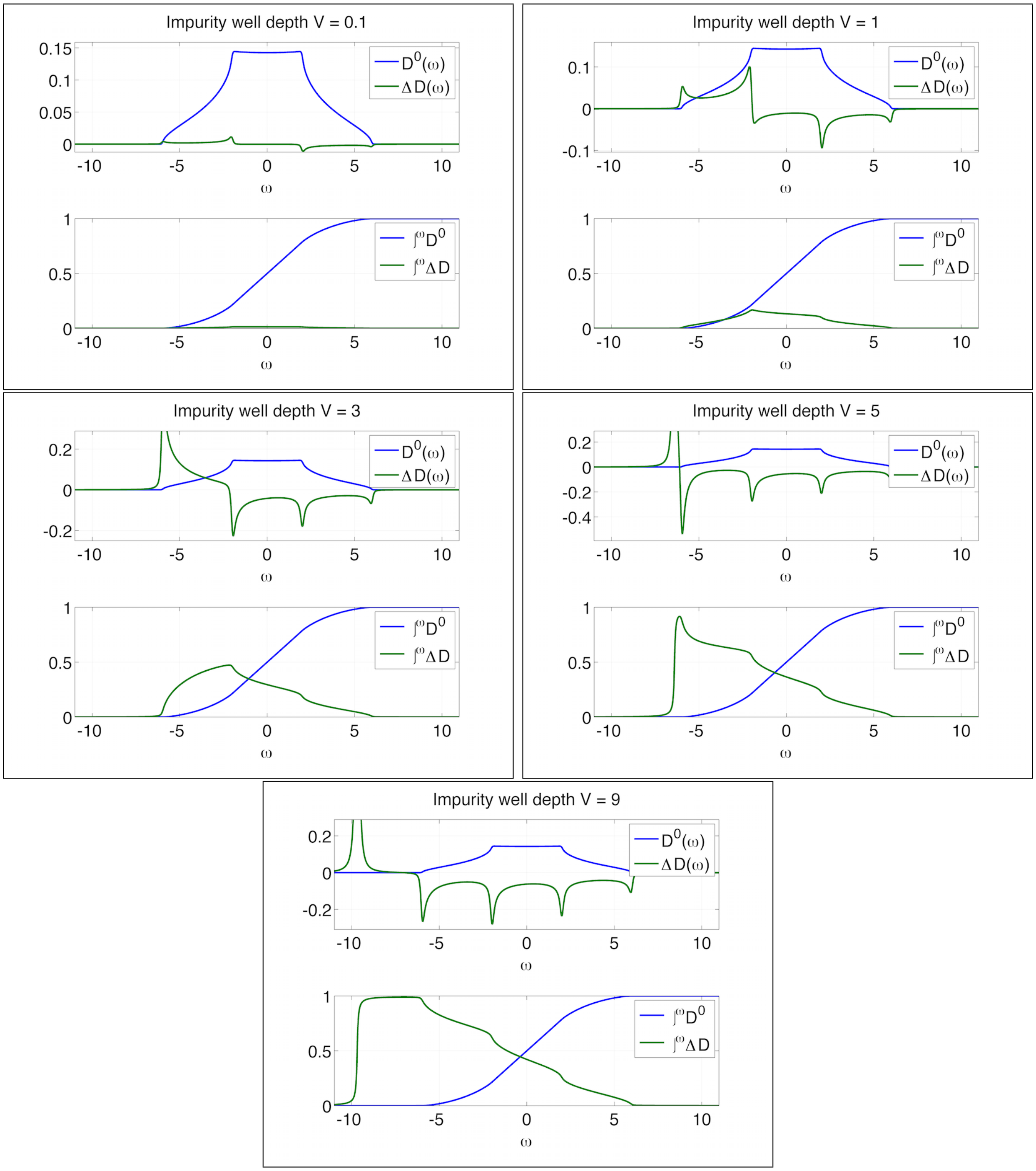
which is just first order perturbation theory: if all states move down by V in energy (since all originally delocalized wave states have same interaction with the localized well $-V$ at the origin), then the change in DOS should be the derivative of the DOS times V since we just shift the DOS along the energy axis. Nevertheless, we get a general enhancement of the DOS at all energies. For large V, the integral starts at essentially one at the lower band edge (since we have the bound state already integrated up) and then decreases over the band; it hits a value very close to 1/2 at $\mu_0 = 0$ in the middle of the band where $R(0) = 0$.

3.1 Meaning of partial doping

The results in the previous section show that a defect that is in principle a donor may not actually end up donating all its electrons to the conduction band even if there is no bound state formed. The change of density of states also accommodates electrons. Here we want to make these thoughts a bit more precise and based on a real-space (localized) view instead of just the aggregate density of states D_{tot} and its overall change ΔD_{tot}.

We return to the relation

$$D_{tot}(\omega) = \sum_\alpha D(\omega,\alpha) = \sum_\alpha \left[D^0(\omega) + \Delta D(\omega, r_\alpha)\right] = N D^0(\omega) + \sum_\alpha \Delta D(\omega, r_\alpha)$$


Impurity well depth V = 0.1

Impurity well depth V = 1

Impurity well depth V = 3

Impurity well depth V = 5

Impurity well depth V = 9

Figure 4: Unperturbed density of states per site $D^0(\omega)$ and the change in total density of states of the entire lattice $\Delta D(\omega)$ for the simple cubic nearest neighbor system for a range of impurity well depths V. For each V, the top panels shows the densities of states while the bottom panel shows their cumulative integrals.

so we have the obvious conclusion that the total change of the DOS is the sum of the changes of all the LDOS

$$\Delta D_{tot}(\omega) = \sum_{\alpha} \Delta D(\omega, r_\alpha)$$

and in the case of our impurity we have the specific form for change of LDOS

$$\Delta D(\omega, r_\alpha) = \frac{1}{\pi} Im \left[\frac{V g(\omega, r_\alpha)^2}{1 + g(\omega)V} \right] .$$

Note that in what follows we are much more interested in the integrals of the changes of the LDOS up to the unperturbed Fermi level

$$\int^{\mu_0} \Delta D(E, r_\alpha) dE \, .$$

It is physically sensible that the change on LDOS $\Delta D(\omega, r_\alpha)$ is localized around the impurity site: the perturbation effect on the LDOS due to the impurity does not extend out to infinity so that far way the material is unperturbed in terms of electronic structure. For example, the data in Figure 5 show that the changes of LDOS are quite localized around the impurity and the sum over only a few shells of lattice sites around the impurity gives already a very good approximation to the total change D_{tot}. In fact, the LDOS on the impurity site alone already delivers quite a good approximation in terms of the overall shape and magnitude over all ω of $\int^{\omega} \Delta D_{tot}$. Therefore we will be assuming that these changes are localized.

Hence, far from the defect site, the LDOS is unchanged from the ideal DOS per site $D^0(\omega)$. Therefore, the change of local electron density (electron number) n on a site far away from the defect is simply the unperturbed DOS at the unperturbed Fermi times the change of Fermi level:

$$\Delta n_{far} = \Delta\mu \cdot D^0(\mu_0) = \frac{1}{N} \cdot \left(\delta - \int^{\mu_0} \Delta D_{tot}(E) dE \right) .$$

The naive result would have been to expect $\Delta n_{far} = \delta/N$ where all the donated electrons would spread evenly throughout the lattice. The only time this generically will happen is when there is no bound state below the band edge and μ_0 is at or below the band edge so the integral is null: namely, an insulator where we have a donor giving all δ electrons to delocalized states right at the conduction band edge. In this case, we may be changing the DOS in the conduction band but it is not relevant: we donate δ electrons to a thermodynamically large conduction band density of states and the band edge states are delocalized states (like all the band states) and thus the δ electrons wander away in these delocalized states.

However, once we have a Fermi level μ_0 that is actually inside the band, we do not expect to get δ/N doping per site but something smaller due to the change of the density of states. If have a bound state develop below the band edge and we have an initially insulating system, then we don't get any doping at all since δ equal the integrals of ΔD_{tot} over the bound state energy — i.e., at zero temperature, the donor bound state is not ionized so no electrons are liberated into the conduction band.

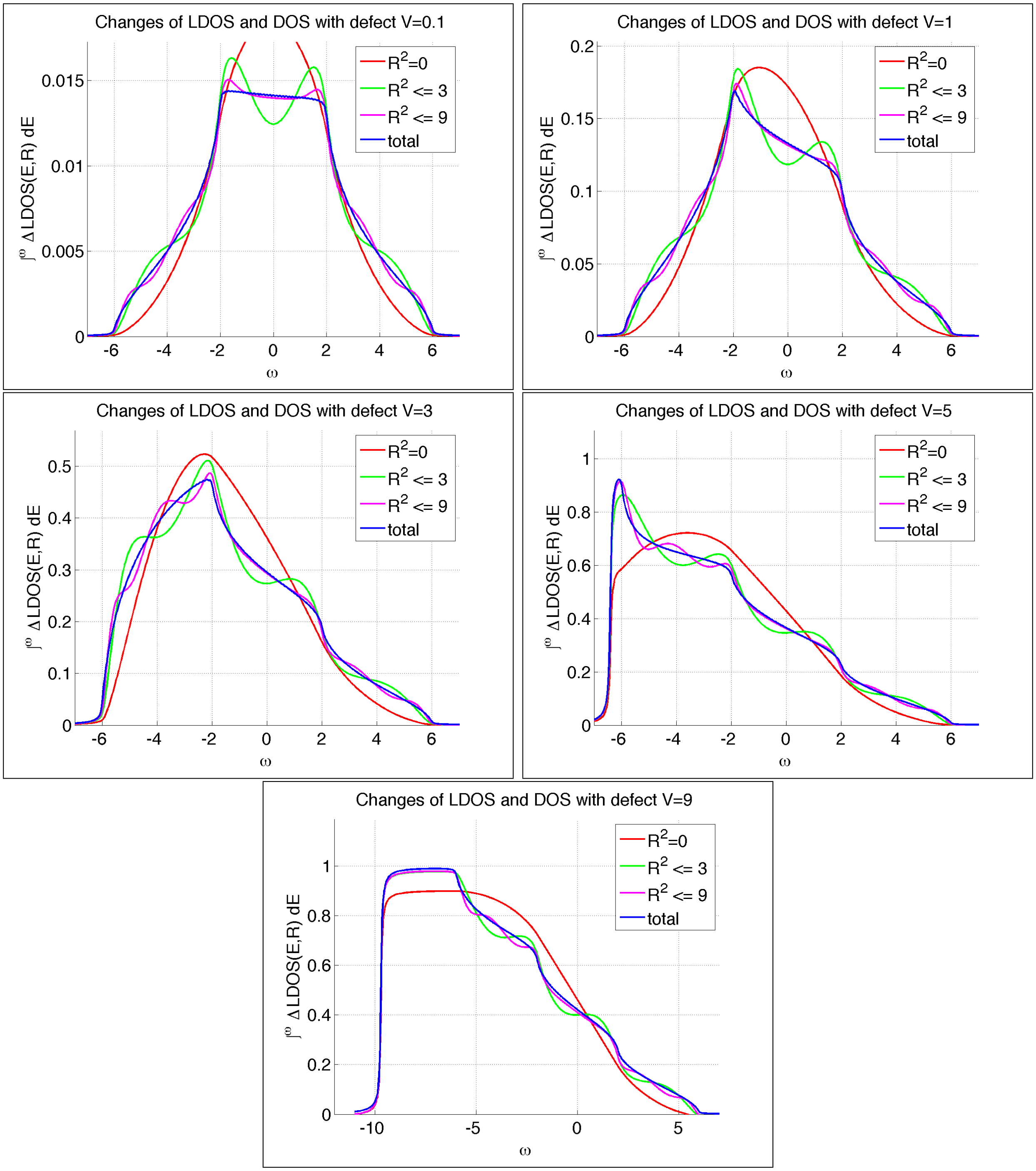


Figure 5: Integrals of the (sums of) changes of LDOS $\Delta D(E, r_\alpha)$ from $-\infty$ to ω for the impurity site ($R^2 = 0$), all sites with $R^2 \leq 3$ (i.e. 000, 100, 110, and 111), and all sites with $R^2 \leq 9$. The integral of the total change of DOS ΔD_{tot} is also shown. A range of impurity well depths V are described.

We must keep in mind that the change of density of states ΔD_{tot} is localized around the impurity: the enhanced localized LDOSs up to μ_0 can "eat up" some fraction of the dopant electrons δ around the impurity reducing the ones that are "liberated" into the lattice. How large this effect is in practice depends on the strength of the impurity well: as Figure 5 shows, it can be as small as ~ 0.01 lost states (bands) per site up to ~ 0.5 lost states (bands) per site for μ_0 somewhere inside the band and not close to the lower or upper band edges.

4 Impurity wells and cut bonds

Here we study some slightly more complex defects (more realistic in some sense). We take our cubic lattice of s orbitals and cut one bond between two neighboring orbitals (i.e., set $t = 0$). This creates two adjacent sites which have connectivity of 5 instead of 6. In addition, we may lower the potential of the two sites to create a well as well. This is an extremely simplified way to understand the behavior of an oxygen vacancy in a metallic perovskite oxide such as $LaNiO_3$. The partially filled conduction band is composed of Ni d orbitals and the Ni live on a cubic sub lattice. Each pair of neighboring Ni atoms is connected via an oxygen atom: it is the Ni-O overlap that leads to the effective Ni-O-Ni hopping which we are calling t. We completely ignore the orbital structure of the multiple d states on the Ni and replace them by a single s orbital. When an oxygen is removed, the hopping between the two neighboring Ni atoms is essentially gone, and since O are anions, electrostatics should make the two "exposed" Ni sites more favorable for electrons; in addition, the missing anti-bonding level repulsion also lowers the two Ni on site energies.

We will not attempt to solve this model analytically but simply present numerical results. These are shown in Figure 6. The figures are quite information rich, so we only pick out some basic facts.

First, cutting the bond between sites (d,0,0) and (d+1,0,0) only changes the LDOS very weakly at these sites and negligibly at other sites. There is an overall band narrowing both on the defect sites and more generally: suppressed DOS at band edges and enhanced in the center. But the effects is quite weak.

Second, the effects are quite localized in space for weak and strong well depths. The strongest effect on the LDOS is on a defect site (d+1,0,0) as expected, the next site (d+2,0,0) is also perturbed, but farther site LDOS are hardly modified.

Third, for strong potential wells, we see two bound states appear. This make sense since we have two defect sites and each defect site in a 3D lattice of this sort can give one bound state. They are split in energy which means a symmetric/antisymmetric pair of bound states.

Fourth, for very weak or quite strong potential wells, the modification to the DOS inside the energy band is quite weak: either there is no potential to change anything or a deep bound

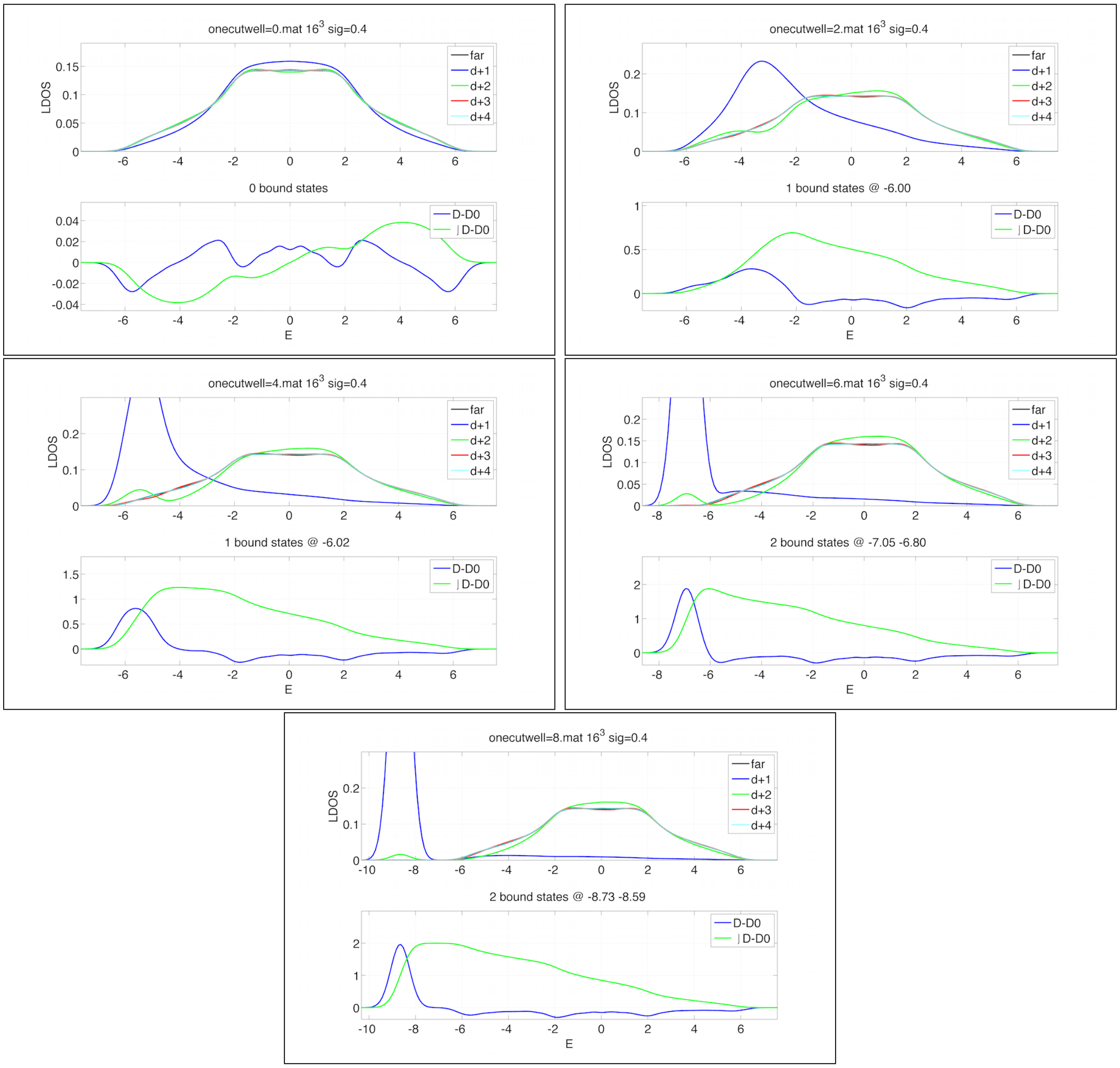


Figure 6: DOS and LDOS for the cubic lattice with $t = -1$ and with one bond removed and energy wells created on the two sites with lower coordination. The well depth is in the title as part of the file name. The defect is created by setting $t = 0$ between sites (d,0,0) and (d+1,0,0) and lowering the on site energies of these two sites. The top panel for each case shows various LDOS: far away (bulk like), and nearby on sites (d+n,0,0). The bottom panel in each case shows the change of total DOS versus energy E and its cumulative integral up to energy E. "sig" refers to the Gaussian broadening use to compute these DOS and LDOS.

states develop that effectively decouple from the lattice. But for intermediate potential wells, we see a strong modification of the LDOS and total DOS in the energy band: the integrated change of DOS is of order unity.

Fifth, the defect sites shows consistent behavior in its LDOS versus energy: as the well depth increase, the (d+1,0,0) LDOS is enhanced at low energies and suppressed at higher energies. The LDOS for the next site (d+2,0,0) is more complex: at the lowest energies it is enhanced but at slightly high energies it is suppressed and at high energies it is enhanced. This is a combination of a few factors: taking advantage of the potential well at low energies, orthogonality to the defect states at low energies, band narrowing as the defect site gets more localized and decouples from the lattice so (d+2,0,0) effectively has a connectivity of 5 instead of 6, and sum rule conservation making for moved spectral weight.

The final set of plots in this document shows the case of two adjacent bond cuts: the hopping between (d,0,0) and (d+1,0,0) is set to zero as is that between (d+1,0,0) and (d+2,0,0). This simulates a pair of neighboring oxygen vacancies along an axial direction. All three sites can also be lowered in energy by a potential well contribution. Notice that site (d+1,0,) has connectivity 4 while the other two have connectivity 5. Figure 7 shows the evolution of the DOS and LDOS in such a system. The general trends observed above for the single vacancy hold here. We observe three bound states developing for deep wells.

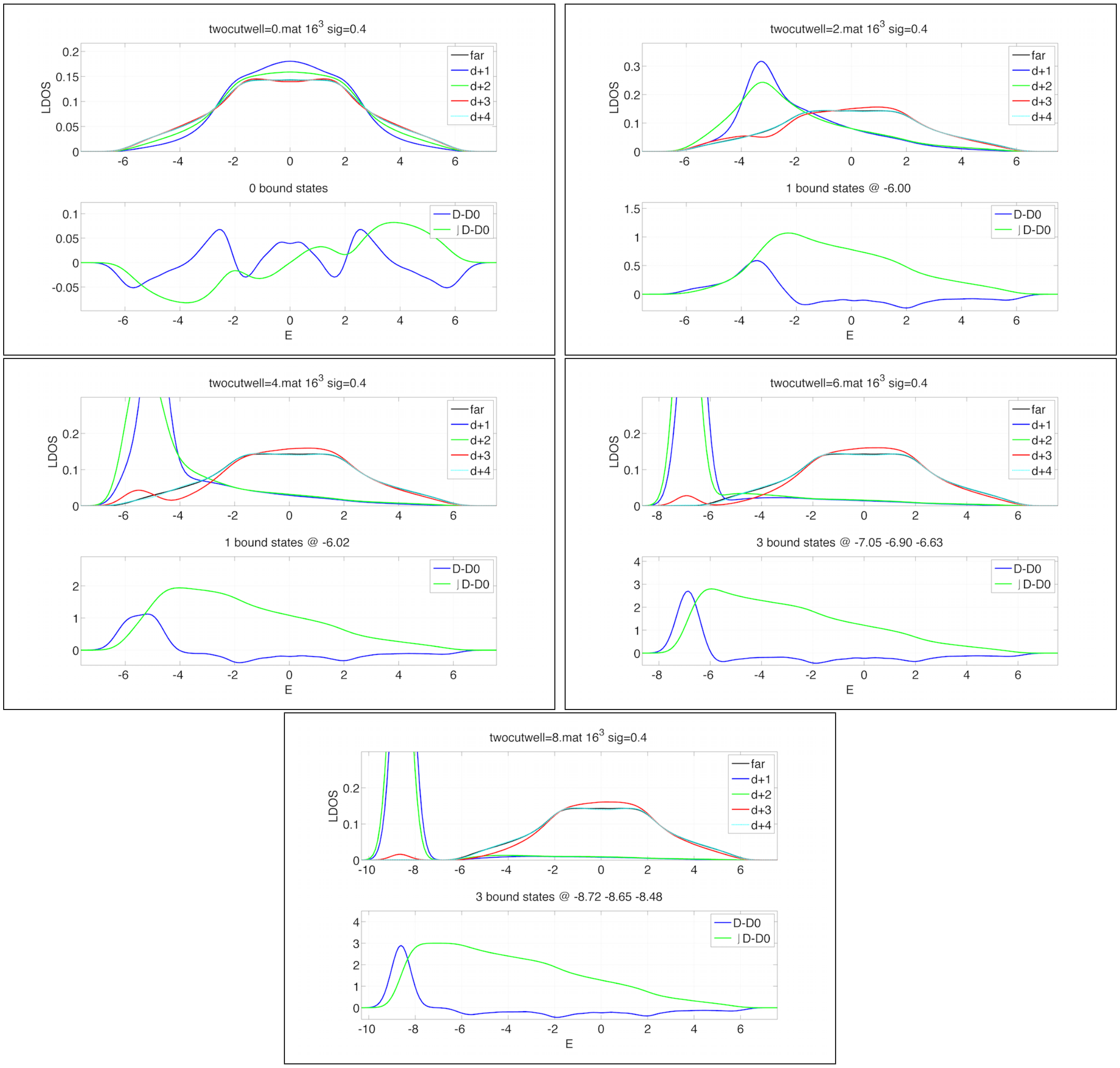


Figure 7: DOS and LDOS for the cubic lattice with $t = -1$ and with two bonds removed and energy wells created on the three sites with lower coordination. The well depth is in the title as part of the file name. The defect is created by setting $t = 0$ between sites (d,0,0) and (d+1,0,0) as well as between (d+1,0,0) and (d+2,0,0) and lowering the on site energies of these two sites. The top panel for each case shows various LDOS: far away (bulk like), and nearby on sites (d+n,0,0). The bottom panel in each case shows the change of total DOS versus energy E and its cumulative integral up to energy E. "sig" refers to the Gaussian broadening use to compute these DOS and LDOS.