

Resolving the chicken-and-egg problem in VO₂: a new paradigm for the Mott transition

O. Nájera,¹ M. Civelli,¹ V. Dobrosavljević,² and M. J. Rozenberg¹

¹*Laboratoire de Physique des Solides, CNRS-UMR8502, Université Paris-Sud, Orsay 91405, France*

²*Department of Physics and National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32306, USA*

We consider a minimal model to investigate the metal-insulator transition in VO₂. We adopt a Hubbard model with two orbital per unit cell, which captures the competition between Mott and singlet-dimer localization. We solve the model within Dynamical Mean Field Theory, characterizing in detail the metal-insulator transition and finding new features in the electronic states. We compare our results with available experimental data obtaining good agreement in the relevant model parameter range. Crucially, we can account for puzzling optical conductivity data obtained within the hysteresis region, which we associate to a novel metallic state characterized by a split heavy quasiparticle band. Our results show that the thermal-driven insulator-to-metal transition in VO₂ is entirely compatible with a Mott electronic mechanism, solving a long standing "chicken-and-egg" debate and calling for further research of "Mottronics" applications of this system.

Vanadate systems have remained at center stage of condensed matter physics for a long time. In fact, both vanadium dioxide VO₂ and vanadium sesquioxide V₂O₃ are considered the prototypical examples of systems undergoing a strongly correlated metal-insulator transition (MIT) [1]. These transition metal oxides are not only important from a fundamental physics point of view, as their unusual electronic behavior makes them very attractive materials for novel electronic devices [2, 3]. In fact, they are intensively investigated in the emerging field of "Mottronics", which aims to exploit the functionalities associated to the quantum Mott transitions. A key goal is to create fast and ultra-low power consumption transistors, which may be downsized to the atomic limit [4–6].

Both, VO₂ and V₂O₃ have nominally partially filled bands, hence are expected to be metals. However, they undergo a first order metal to insulator transition upon cooling at $\sim 340\text{K}$ and 180K , respectively. Significantly, this phenomenon has been associated, time and again, to a Mott transition [1], namely a metal-insulator transition driven by the competition between kinetic energy and Coulomb electric repulsion [7]. Yet, that point of view has also been questioned, almost as often [1, 8].

The case of VO₂, that has a transition from a high- T rutile (R) metallic phase to a low- T monoclinic (M₁) insulator, is emblematic. The debate started with the seminal works of Morin and Goodenough [9–11] more than 50 years ago and remains ongoing [12–16]. While many features are currently open for debate, the half-century-long central issue is the nature of the transition and the role of strong correlations effects. More specifically, whether the transition is essentially driven by a band-structure effect due to a spin-Peierls structural instability, or by the electronic charge localization of the Mott-Hubbard type. This issue has been under scrutiny using realistic electronic structure calculations [17–21] based on the combination of Density Functional Theory with Dynamical

Mean Field Theory (LDA+DMFT) [22]. In a pioneering attempt to solve the problem, Biermann et al. [17] argued that the metal-insulator transition should be considered as a renormalized Peierls insulator. Namely, a band-insulator where the bonding-antibonding bandgap is driven by dimerization and renormalized down by interactions [17]. Specifically, they observed that within the monoclinic phase, the splitting of the a_{1g} bonding-antibonding bands is renormalized from the value ~ 1.5 eV within the LDA, down to ~ 0.8 eV when a Hubbard repulsion term is included. On the other hand, the calculations showed that within the metallic rutile phase, the Coulomb interaction failed to produce a MIT for reasonable values of the interaction. These calculations, done more than 10 years ago, provided multiple insights even if they were done at the high temperature of 770 K. More recently, the problem was reconsidered by Brito et al. [19] and by Biermann et al. as well [20, 23–25]. Although they employed similar techniques, their results and emerging scenario is rather different. Brito et al. found a MIT within a second monoclinic (M₂) phase of VO₂ that only has half the dimerization of the standard M₁, for the same value of the Coulomb interaction. Hence, they argued that Mott localization must play the leading role in both MITs. Nevertheless, they also noted that the Mott insulator adiabatically connects to the singlet dimer insulator state, and therefore the transition should be considered as a Mott-Hubbard in the presence of strong inter-site exchange [19, 20, 23].

While those LDA+DMFT works provided multiple useful insights, the issue whether the first order MIT at 340K in VO₂ is electronically or structurally driven, still remains. Thus, here we shall try to shed new light on this classic "chicken-and-egg" problem by adopting a different strategy. We shall avoid the complications of the realistic crystal structures and orbital degeneracy of VO₂ and adopt a basic model Hamiltonian that permits a detailed systematic study. The model is a lattice Hubbard

Hamiltonian with hopping t and Coulomb repulsion U , which has a two orbital dimer per unit cell with intra-cell hopping t_{\perp} [26]. Significantly, the quantum impurity problem of this model treated within DMFT is *analogous* to that of the above mentioned LDA+DMFT studies [17, 19, 20, 23](cf Supplemental Material). This model Hamiltonian, which we shall call Dimer Hubbard model (DHM), can capture the competition between Mott localization due to Coulomb repulsion and singlet dimerization, i.e. Peierls localization. We should emphasize here that the underlying lattice in this model *stays put*. Therefore, we can directly address the issue whether a purely electronic transition, having a bearing on the physics of VO₂, exists in this model. The specific questions that we shall address are the following: (i) Does this purely electronic model predict a first order metal-insulator transition as a function of the temperature *within the relevant parameter region*? If yes, (ii) What is the physical nature of the different states? and, (iii) Can they be related to key available experiments? These issues are relevant, since if even this basic model fails to predict an electronic MIT consistent with the one observed in VO₂, then it would be mandatory to explicitly include the lattice degrees of freedom, and the chicken-and-egg question would be resolved. In the present study we shall provide explicit answers to these questions. Specifically, we shall show that the solution of the DHM shall bring the equivalent physical insight for VO₂ as what was obtained with the single band Hubbard model for V₂O₃, which was one of the significant achievements of DMFT [27, 28]. In fact, both models are closely related, as the DHM becomes two identical copies of the single-band Hubbard model at $t_{\perp}=0$.

The dimer Hubbard model is defined as

$$H = [-t \sum_{\langle i,j \rangle \alpha \sigma} c_{i\alpha\sigma}^{\dagger} c_{j\alpha\sigma} + t_{\perp} \sum_{i\sigma} c_{i1\sigma}^{\dagger} c_{i2\sigma} + h.c.] + \sum_{i\alpha} U n_{i\alpha\uparrow} n_{i\alpha\downarrow} \quad (1)$$

where $\langle i, j \rangle$ denotes n.n. lattice sites, $\alpha = \{1, 2\}$ denote the dimer orbitals, σ is the spin, t is the lattice hopping, t_{\perp} is the intra-dimer hopping, and U is the Coulomb repulsion. For simplicity, we adopt for the model a semi-circular density of states $\rho(\varepsilon) = \sqrt{4t^2 - \varepsilon^2} / (2\pi t^2)$. The energy unit is set by $t=1/2$, which gives a full bandwidth of $4t=2D=2$, where D is the half-bandwidth. This interesting model has surprisingly received little attention, and only and partial solutions have been obtained within DMFT [26, 29–31]. The main results were the identification of region of coexistent solutions at moderate U and small t_{\perp} . Those were obtained at $T=0$ using the IPT approximation [26] and at finite $T=0.025$ by quantum Monte Carlo [32, 33] (QMC) [29]. Here, we shall obtain the detailed solution of the problem in the full parameter space, paying special attention to the MIT and the nature of the coexistent solutions. We solve for the DMFT

equations with hybridization-expansion continuous-time quantum Monte Carlo (CT-QMC) [34, 35] and exact diagonalization, which provide (numerically) exact solutions [27]. We also adopt the IPT approximation [26], which, remarkably, we find is (numerically) exact in the atomic limit $t = 0$ (see Supplemental Material), therefore provides reliable solutions of comparable quality as in the single-band Hubbard model [27]. Furthermore, IPT is extremely fast and efficient to explore the large parameter space of the model and provides accurate solutions on the real frequency axis. Extensive comparison between IPT and the CT-QMC is shown in the Supplemental Material. The DMFT equations provide for the exact solution of the DHM in the limit of large lattice coordination and have been derived elsewhere [26]. Here we quote the key self-consistency condition of the associated quantum dimer-impurity model,

$$\mathbf{G}^{-1}(i\omega_n) + (i\omega_n) = \begin{pmatrix} i\omega_n & -t_{\perp} \\ -t_{\perp} & i\omega_n \end{pmatrix} - t^2 \mathbf{G}(i\omega_n), \quad (2)$$

where $G_{\alpha,\beta}$ and $\Sigma_{\alpha,\beta}$ (with $\alpha, \beta = 1, 2$) are respectively the dimer-impurity Green's function and self-energy. At the self consistent point these two quantities become the respective local quantities of the *lattice* [27].

We start by establishing the detailed phase diagram, which we show in Fig. 1. We observe that at low T there is a large coexistent region at moderate U and t_{\perp} below 0.6 [26]. This region gradually shrinks as T is increased, and fully disappears at $T \approx 0.04$. The lower panel shows the phase diagram in the U - T plane at fixed t_{\perp} . At $t_{\perp}=0$ we recover the well known single-band Hubbard model result, where the coexistent region extends in a triangular region defined by the lines $U_{c1}(T)$ and $U_{c2}(T)$ [27]. The triangle is tilted to the left, which indicates that upon warming the correlated metal undergoes a first order transition to a finite- T Mott insulator. This behavior was immediately associated to the famous 1st order MIT observed in *Cr-doped* V₂O₃ [27, 36], which has been long considered a prime example of a Mott Hubbard transition [1]. It is noteworthy that this physical feature has remained relevant even in recent LDA+DMFT studies, where the full complexity of the lattice and orbital degeneracy is considered [8, 37]. This underlines the utility of sorting the detailed behavior of basic model Hamiltonians. Significantly, as t_{\perp} is increased in the DHM, the tilt of the triangular region evolves towards the right. This signals that t_{\perp} fundamentally changes the stability of the groundstate. In fact, as shown in the lower right panel of Fig. 1, at $t_{\perp}=0.3$ we find that the MIT is *reversed* with respect to the previous case, namely, upon warming, an insulator undergoes a 1st order transition to a (bad) correlated metal at finite- T . Interestingly, we may connect several features of this MIT to VO₂, both, qualitative and quantitatively. Firstly, we may consider the energy scales. The LDA estimate of the bandwidth of the metallic state of VO₂ is $\sim 2\text{eV}$ [17], which corresponds in our

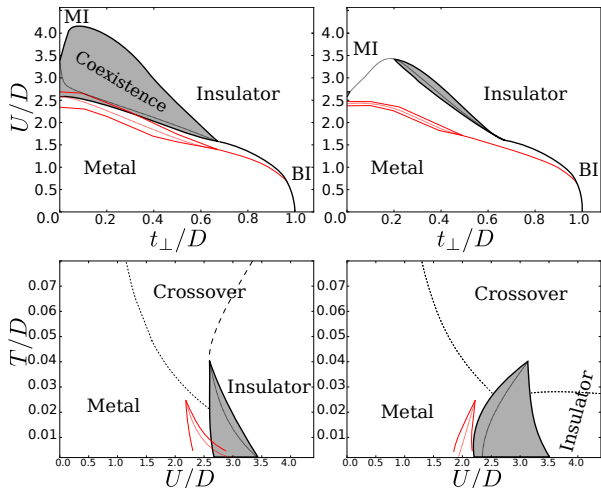


Figure 1. Phase diagram showing the coexistence (grayed) of metal and insulator states (black lines from IPT and red from QMC), where the approximate position of the 1st order lines is indicated. MI denotes Mott insulator and BI bond insulator, the crossover regions have bad metal behavior (see text and Ref.40). Top panels show t_{\perp} - U plane. Left one shows lower temperatures $T=0.001$ (IPT) and $1/200$ (CT-QMC), and right one shows higher temperature $T=0.03$ (IPT) and $1/64$ (CT-QMC). Lower panels show the U - T plane. Left one is for fixed $t_{\perp}=0$ (i.e. single-band Hubbard model), and right one for $t_{\perp}=0.3$.

model to $4t$, hence $t=0.5\text{eV}$. This is handy, since from our choice of $t=0.5$, we may simply read the numerical energy values of the figures directly in physical units (eV) and compare to experimental data of VO_2 . Moreover, the value of the tight binding parameter $t_{\perp}=0.3$, that corresponds to 0.3eV is consistent with LDA estimates for the (average) intra-dimer hopping amplitudes (cf Supplemental Material) [38, 39]. Interestingly, from Fig. 1 we find that the coexistent solution region at $t_{\perp}=0.3$, hence the 1st order transition, extends up to a $T_{MIT} \approx 35\text{meV} \approx 400\text{K}$, consistent with the experimental value $\approx 340\text{K}$. Furthermore, this occurs for a value of the Coulomb repulsion $U \approx 2 \sim 3\text{eV}$, also quite consistent with the values adopted in the LDA+DMFT studies [17, 19, 38].

We can make further interesting connections with experiments in VO_2 . The metallic state is unusual and it can be characterized as a *bad metal*. Namely, a metal with an anomalously high scattering rate that approaches (or may violate) the Ioffe-Regel limit [41]. In Fig. 2 we show the imaginary part of the diagonal self-energy, whose y-axis intercept indicates the scattering rate (i.e. inverse scattering time). At $T \approx 0.04$ (i.e. $\sim 400\text{K}$) we observe a large value of the intercept, of order $\sim t=1/2$, which signals that the carriers are short lived quasiparticles. In fact VO_2 has such an anomalous metallic state [12]. This anomalous scattering is likely the origin of the surprising observation that despite the fact that the lattice structure has 1D vanadium chains run-

ning along the c-axis, the resistivity is almost isotropic, within a mere factor of 2 [11]. It is noteworthy that this lack of anisotropy observed in electronic transport experiments provides further justification for our simplified model of a lattice of dimers. Thus, this bad metal behavior, which is a hallmark of Mottness [40, 42], also indicates that the MIT in VO_2 should be characterized as a Mott transition[?]. Additional insights on the mechanism driving the transition can be obtained from the behavior of the off-diagonal (intra-dimer) self-energy $\Sigma_{12}(\omega_n)$. From Eq. (2), we observe that the intra-dimer hopping amplitude is effectively renormalized as $t_{\perp}^{eff} = t_{\perp} + \Re[\Sigma_{12}](0)$. In Fig. 2 we show the behavior of this quantity across the transition. We see that in the metallic state it remains very small, while it becomes large ($\gg t_{\perp}$) at low T in the insulator [19, 20, 23]. The physical interpretation is transparent. In the correlated metal, the two dimer sites are primarily Kondo screened by their lattice neighbors, as in the single band Hubbard model each one forms a heavy quasiparticle band. Then these two bands get split into a bonding and anti-bonding pair by the small t_{\perp} . Hence, the low energy electronic structure is qualitatively similar to the non-interacting one, with a larger effective mass. As T is lowered, the dramatic increase in $\Re[\Sigma_{12}](0)$ when the Mott gap opens at the 1st order transition signals that the intra-dimer interaction is boosted by $\propto t_{\perp}^{eff} \sim \Re[\Sigma_{12}]$. Unlike the one-band Hubbard model, here the finite t_{\perp} permits a large energy gain in the Mott insulator by quenching the degenerate entropy. This mechanism, already observed in other cluster-DMFT models [43–45], stabilizes the insulator within the coexistence region, leading to the change in the tilt seen in Fig.1. Another way of rationalizing the transition is that at a critical U -dependent t_{\perp} the Kondo screening in the metal breaks down in favor of the local dimer-singlet formation in the insulator. In this view, the large gap opening may be interpreted as a U -driven enhanced band splitting $\propto 2t_{\perp}^{eff}(U)$.

Further detail is obtained from the comparison of the electronic structure of the metal and the insulator within the coexistence region [?]. Within DMFT, the bandstructure is obtained as a function of the single particle energy ϵ , which in the semicircular DOS lattice adopted here has a simple linear dispersion [27]. Hence at $U=0$ the non-interacting bandstructure are two parallel linear bands split by $2t_{\perp}$ (i.e. the bonding and anti-bonding bands). In the correlated metallic state shown in Fig. 3 we find at high energies ($\sim \pm U/2$) the incoherent Hubbard bands, which are signatures of Mott physics. At lower energies, we also observe a pair of heavy quasiparticle bands crossing the Fermi energy at $\omega=0$. Consistent with our previous discussion, this pair of quasiparticle bands can be thought of as the renormalization of the non-interacting bandstructure. Significantly, as we shall discuss later on, this feature may explain the puzzling optical data of Qazilbash et al. [12] within the MIT region

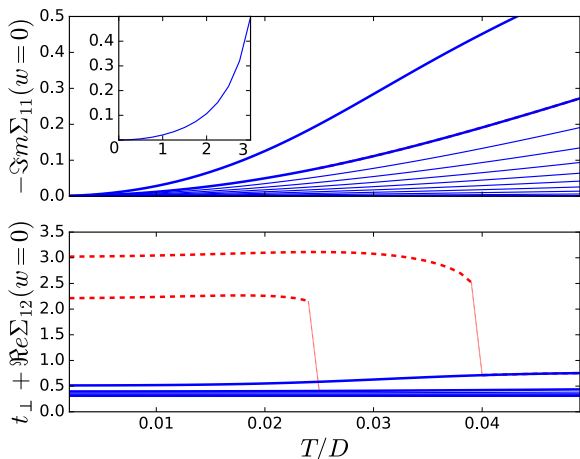


Figure 2. Top: The scattering rate $\text{Im}[\Sigma_{11}(\omega = 0)]$ for the metal (solid) at fixed $t_{\perp}=0.3$ values of U from 0 to 3 in steps of 0.5 (upwards). The experimentally relevant values $U=2.5$ and 3, are highlighted with thick lines. Inset shows the U dependence at fixed $T=0.04$. Bottom: The effective intradimer hopping $t_{\perp}^{eff} = t_{\perp} + \text{Re}[\Sigma_{12}](0)$ (bottom) as a function of T for the same parameters as the top panel. Metal states are in solid (blue) lines and the insulator in dashed (red) lines for $U=2.5$ and 3. The calculation are done with IPT.

of VO_2 , which has remained unaccounted for so far. Unlike the single-band Hubbard model, the effective mass of these metallic bands does not diverge at the MIT at the critical U , even at $T=0$. In fact, the finite t_{\perp} cuts off the effective mass divergence as expected in a model that incorporates spin-fluctuations. In fact the DMH may be considered [26] the simplest non-trivial cluster DMFT model. It is interesting to note that the realistic values $U = 2.5$ and $t_{\perp} = 0.3$ lead to Hubbard bands at $\approx \pm 1.5\text{eV}$ and a quasiparticle residue $Z \approx 0.4$, both consistent with photoemission experiments of Koethe et al. [46].

In Fig. 3 we also show the results for insulator electronic dispersion at the same values of the parameters. The comparison of the insulator and the metal illustrate the significant changes that undergo at the 1st order MIT. We see that the metallic pair of quasiparticle band suddenly open a large gap. More precisely, in contrast to the one-band case, here the Hubbard bands acquire a non-trivial structure, with sharp bands coexisting with incoherent ones. The coherent part dispersion can be traced to those of a lattice of singlet-dimers (see Sup. Mat.). Hence, the insulator can be characterized as a novel type of Mott-singlet state where the Hubbard bands have a mix character with both coherent and incoherent electronic-structure contributions. It is also interesting to note that the gap in the density of states is $\Delta \approx 0.6\text{eV}$, again consistent with the photoemission experiments [46].

In order to gain further insight and make further con-

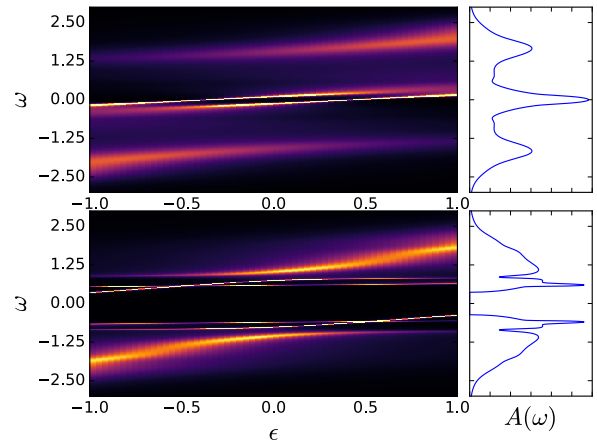


Figure 3. Electronic dispersion for the metal (left top) and insulator (left bottom) in the coexistence region for parameter values $t_{\perp}=0.3$, $U=2.5$ and $T=0.01$. Right panels show the respective DOS(ω). The calculations are done with IPT.

tact with key experiments, we now consider the optical conductivity response $\sigma(\omega)$ within the MIT coexistence region. A set of remarkable data was obtained in this regime by Qazilbash et al. [12], bearing directly on the issue of the driving force behind the transition. They systematically investigated the $\sigma(\omega)$ as a function of T using nano-imaging spectroscopy. They clearly identified within the T range of the MIT the electronic coexistence of insulator and metallic regions, characteristic of a 1st order transition. A crucial observation was that upon warming the insulator in the M1 phase, metallic puddles emerge with a $\sigma(\omega)$ that was significantly different from the signal of the normal metallic R phase. Thus, the data provided a strong indication of a purely electronic driven transition. Regarding this point we would like to mention also the works of Arcangeletti et al. [15] and Laverock et al. [16] that reported the observation of metallic states within the monoclinic phase under pressure and strain, respectively. Coming back to the experiment of Qazilbash et al., a key point that we want to emphasize here is that $\sigma(\omega)$ in the putative M1-metallic state was characterized by a intriguing mid-infra-red (MIR) peak $\omega_{mir} \approx 1800 \text{ cm}^{-1} = 0.22 \text{ eV}$, whose origin was not understood. From our results on the electronic structure within the coexistence region, we find a natural interpretation for the puzzling MIR peak: It should correspond to excitations between the split metallic quasiparticle bands. Since they are parallel, they would produce a significant contribution to $\sigma(\omega)$, which enabled its detection. In Fig. 4 we show the calculated optical conductivity response (see Sup. Mat. section 7) that corresponds to the spectra of Fig. 3. In the metal we see that, in fact, a prominent MIR peak is present at $\omega_{mir} \approx 0.22 \text{ eV}$, in excellent agreement with the experimental value. On the other hand, the optical conductivity of the insulator shows a maximum at

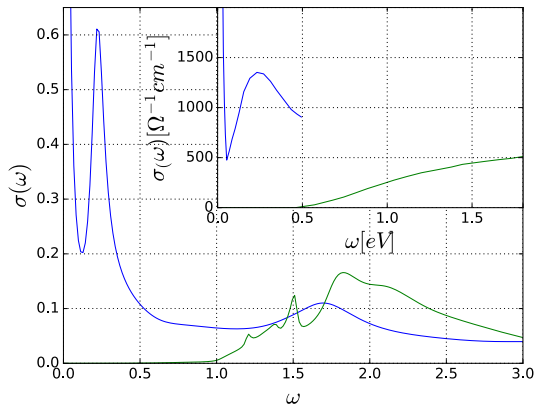


Figure 4. The optical conductivity $\sigma(\omega)$ of metal and insulator within the coexistence region for parameters $t_{\perp}=0.3$, $U=2.5$ and $T=0.01$. The calculations are done with IPT. Inset: The experimental optical conductivity adapted from Ref. 12.

$\omega_{ins} \approx 2$ eV in both, theory and experiment. Moreover, we also note the good agreement of the relative spectral strengths of the main features in the two phases.

In conclusion, we showed that the detailed solution of a minimal dimer model treated within DMFT can successfully account for a number of experimental features observed in VO_2 . The minimal model has an impurity problem which is analogue to that of LDA+DMFT methods, yet the simplicity of this approach allowed for a detailed solution that permitted a transparent understanding of many physical aspects of the electronic first order transition in this problem. It exposed a novel dimer-Mott-transition mechanism, where the effective intra-dimer exchange is controlled by correlations, it is weakened in the metal and strongly enhanced in the Mott insulator. In the metal, this leads to a pair of split quasiparticle bands, which then in the insulator further separate, to join and coexist with the usual incoherent Hubbard bands. We made semi-quantitative connections to several experimental data in VO_2 , including a crucial optical conductivity study within the 1st order transition, that remained unaccounted for. Our work, sheds new light on the long-standing question of the driving force behind the metal-insulator transition of VO_2 , indicating that it is driven by a Mott mechanism. The present approach may be considered the counterpart for VO_2 , of the DMFT studies of the Mott transition in paramagnetic Cr-doped V_2O_3 .

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Supplementary Material

DIMER HUBBARD MODEL REPRESENTATION

In figure S1 we show on the left panel the schematic representation of our model Hamiltonian. The blue lines correspond the inter-dimer hopping matrix \mathbf{t} and the purple line the intra-dimer hopping \mathbf{t}_\perp . For simplicity the model is depicted in 3D, but it is mathematically formulated in the limit of a large coordination lattice. The right hand side panel shows the corresponding DMFT quantum impurity problem, where the dimer is embedded in a self consistent medium.

VALIDATION OF IPT AGAINST THE EXACTLY SOLVABLE ISOLATED DIMER LIMIT (IE ATOMIC LIMIT OF THE LATTICE MODEL)

We numerically demonstrate that the IPT method exactly captures the atomic limit of the lattice model. The fact that a perturbative calculation captures the atomic limit (ie, $U/t \rightarrow \infty$) is not to be expected, but, interestingly enough, is analogous to the well known property of the IPT solution of the one band Hubbard model. This is shown

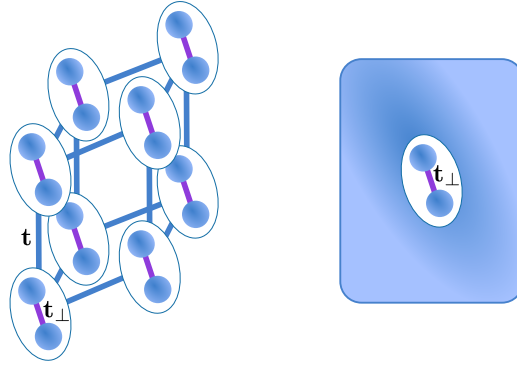


Figure S1. Left panel: schematic representation of the lattice Hamiltonian. Right panel: Associated self-consistent quantum impurity problem, where the dimer is embedded in a self-consistent medium. .

in figure S2 where we compare the exact Self-Energy of the atomic limit (isolated dimer) with the respective IPT solution.

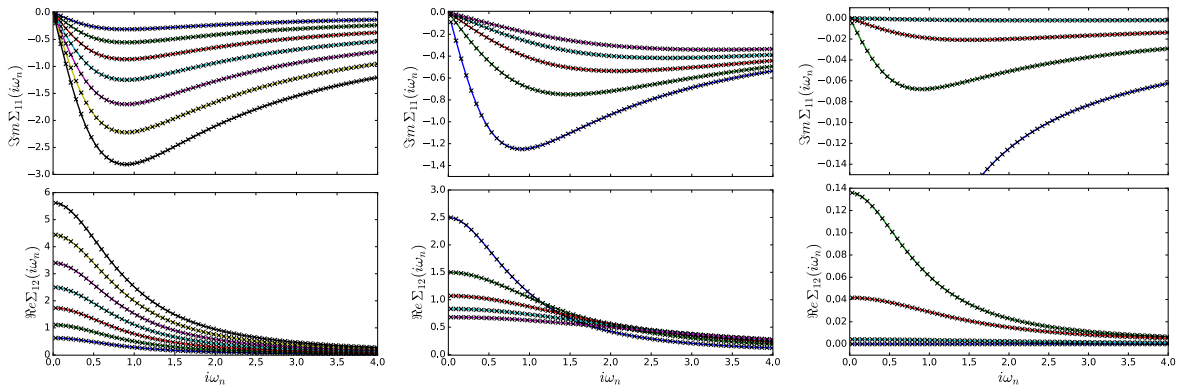


Figure S2. Comparison between the exact Self-Energy of an isolated dimer (solid lines) and the approximation from IPT (black crosses) (Left panel) Self-Energy for various values of U and fixed $t_{\perp} = 0.3$. $U = 1.5$ blue, $U = 2$ green, $U = 2.5$ red, $U = 3$ cyan, $U = 3.5$ purple, $U = 4$ yellow, $U = 4.5$ black. (Center) Various values of t_{\perp} and fixed $U = 3$. $t_{\perp} = 0.3$ blue, $t_{\perp} = 0.5$ green, $t_{\perp} = 0.7$ red, $t_{\perp} = 0.9$ cyan, $t_{\perp} = 1.1$ purple. (Right) Various values of U and t_{\perp} . ($U = 1, t_{\perp} = 0$) blue, ($U = 0.7, t_{\perp} = 0.3$) green, ($U = 0.5, t_{\perp} = 0.5$) red, ($U = 0.2, t_{\perp} = 0.8$) cyan.

COMPARISON OF IPT WITH NUMERICAL SOLUTIONS (CT-QMC AND EXACT DIAGONALIZATION)

Solutions in the Matsubara axis

The most stringent test for the comparison is done within the coexistence region, since there the structure of the Green's functions and Self-Energies are very non-trivial. Figure S3 shows the numerically exact CT-QMC Green's functions and Self-Energies in the Matsubara axis. The data is shown along with fits obtained from the IPT solution at suitably close values of the parameters.

The very good agreement between QMC and IPT is also found in the whole phase diagram. This is shown in figure S4 where IPT and CT-QMC are compared at two parameter values away from the coexistence region.

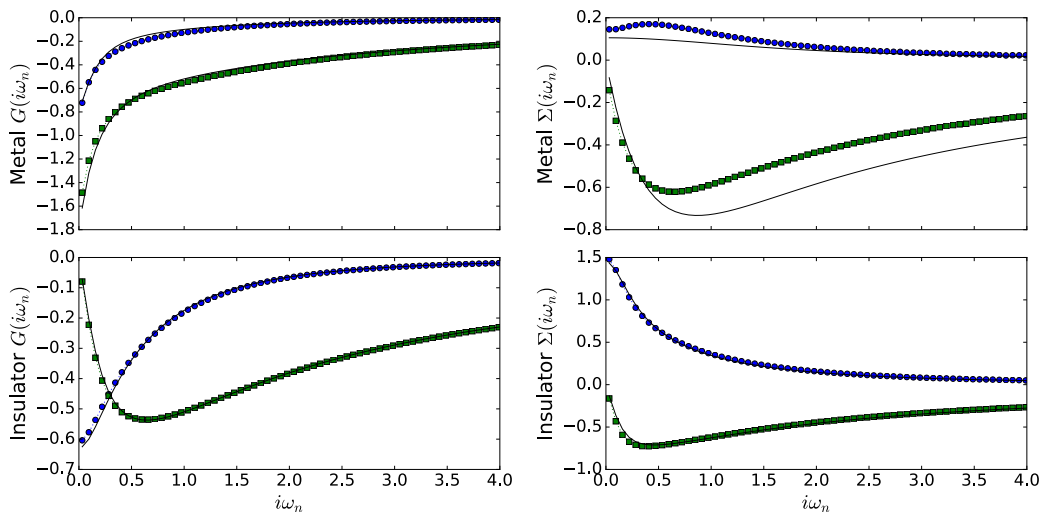


Figure S3. Comparison of the (numerically) exact CT-QMC solution and IPT within the coexistence region for metal (top) and insulator (bottom). Left panels: the local $\text{Im}[G_{11}]$ (green) and $\text{Re}[G_{12}]$ (blue). Right panels: the local $\text{Im}[\Sigma_{11}]$ (green) and $\text{Re}[\Sigma_{12}]$ (blue). Circular and square symbols are CT-QMC data at $U=2.15$ and $t_{\perp}=0.3$, and black solid lines are IPT at $U=2.55$ (metal) and $U=2.21$ (insulator) with $t_{\perp}=0.3$. Notice that, as in the one band Hubbard model case, the best quantitative agreement between QMC and IPT is found for values of U that are slightly different.

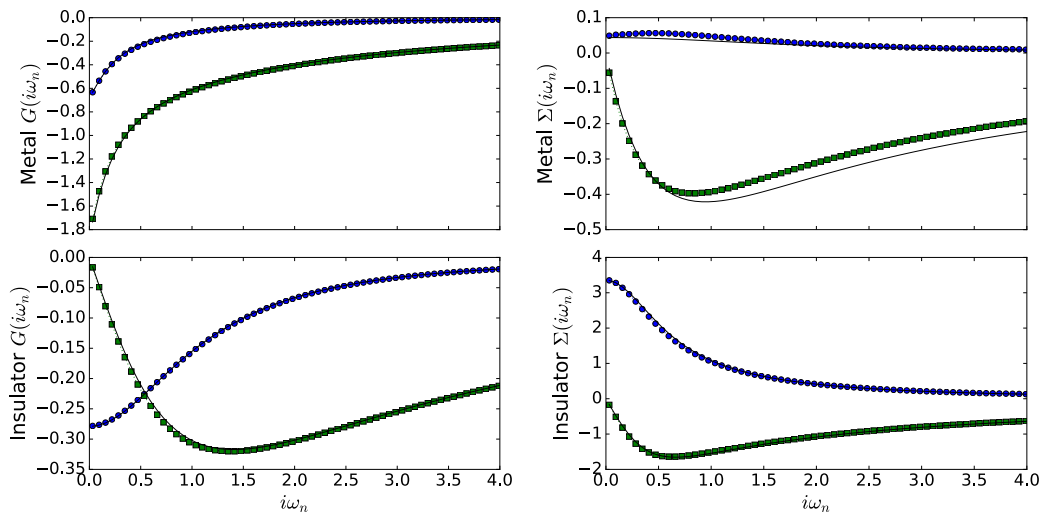


Figure S4. Comparison of the (numerically) exact CT-QMC solution and IPT away from the coexistence region for metal (top) and insulator (bottom). Left panels: the local $\text{Im}[G_{11}]$ (green) and $\text{Re}[G_{12}]$ (blue). Right panels: the local $\text{Im}[\Sigma_{11}]$ (green) and $\text{Re}[\Sigma_{12}]$ (blue). Circular and square symbols are CT-QMC data at $U=1.8$ (metal) and 3.3 (insulator), and black solid lines are IPT at $U=2$ (metal) and 3.35 (insulator). The intra-dimer hopping is always fixed at $t_{\perp}=0.3$. Notice that, as in the one band Hubbard model case, the best quantitative agreement between QMC and IPT is found for values of U that are slightly different.

Electronic Structure

In figure S5 we show the electronic dispersion (ie, ϵ and ω resolved density of states $A(\epsilon, \omega)$) of the metallic and insulating states obtained by the IPT, CT-QMC and ED methods, respectively. As seen in the figure, all the three methods provide the key qualitative features that are discussed in the text. Namely, the split quasiparticle bands in

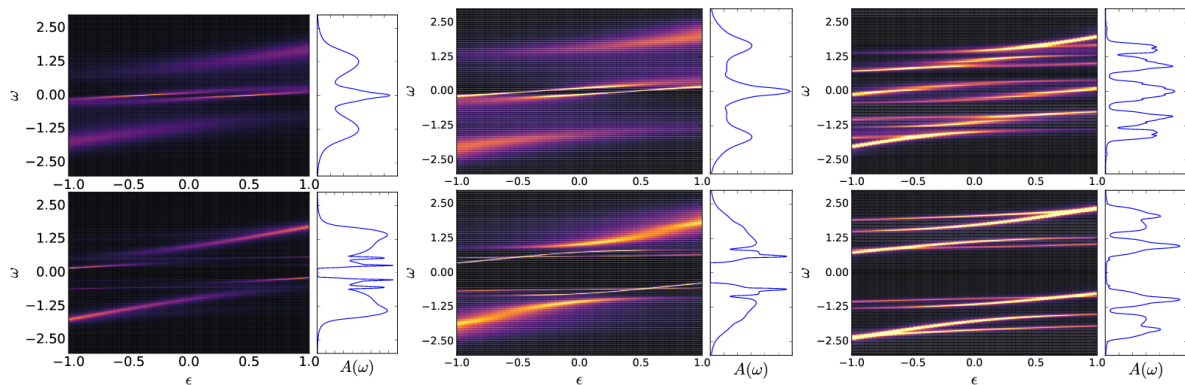


Figure S5. Comparison of the electronic structures in the Metal and Insulator phases at $t_{\perp} = 0.3$. Left CT-QMC in the coexistence $U = 2.15$, center IPT taken from main text $U = 2.5$, right results from ED metal at $U = 1.8$, insulator at $U = 3$

the metal and in the insulating states.

CHOICE OF PARAMETERS IN THE DIMER LATTICE

The dimer Hubbard Model has very few parameters inter-dimer (or lattice) hopping t , intra-dimer hopping t_{\perp} , local Coulomb repulsion U , and the temperature. The lattice hopping provides the bandwidth of our model Hamiltonian $W = 4t$ [S1, S2]. In the case of VO_2 reference LDA calculations agree that both, e_g and a_{1g} bands have an approximate bandwidth of 2eV [S3–S6], hence we have set $t = 0.5\text{eV}$.

The intra-dimer hopping quoted in ref. [S3] is $\sim 0.68\text{eV}$, which is about a factor of 2 larger than our adopted value 0.3eV . However, that value concerns solely the a_{1g} (d_{xy}) orbital. There are in fact also two additional intra-dimer hopping amplitudes (associated to e_g states), which are 0.22eV and a smaller value. The values for the hopping amplitudes found in later works [S4–S6] are consistent with this findings. Since we are considering a unit cell with two sites and one orbital each, we have a single intra-dimer hopping parameter. Therefore, and in the spirit of a mean field theory, we chose a value that is the approximate average of the 3 hopping amplitudes.

In regard to the value of U , we adopted the value of $U = 2.5\text{eV}$ for the semi-quantitative comparison with experiments. This is quite consistent with the values considered in [S6], who systematically explored the range of $U = 2.2$ to 3.5eV , and found the MIT between 2.7 and 3eV at the lowest temperatures considered. The values adopted in ref. [S3, S4] are $U = 4\text{eV}$ and $J = 0.68$. These values are in fact higher than ours, however, Biermann et al dedicate the last paragraph of their Letter to discuss their choice of the value of U and J . They mention that smaller values, such as $U = 2\text{eV}$ are also compatible with their findings. This is also consistent with our choice of $U = 2.5\text{eV}$.

MOTT INSULATOR IN THE DIMER LATTICE

The Mott insulating state is signaled by the divergence of the Self-Energy in the Mott gap. This divergence is clearly visible on the real axis in figure S6(middle and bottom rows). In the left column we show the well known case of a single-band Hubbard model ($t_{\perp} = 0$) with particle-hole symmetry. In this case the Self-Energy diverges at zero frequency, and this is therefore visible in the Matsubara axis too. eg. in figure S2 above (the $t_{\perp} = 0$ blue squares on the top most right panel). In the case of the dimer lattice ($t_{\perp} = 0.3$), with two atoms per unit cell, the dimerization splits the divergence of the Self-Energy into two poles, symmetric around zero frequency, as displayed on the right right column on figure S6. In this case the divergence is no more visible on the Matsubara axis, and in particular $\Im m \Sigma_{11}$ goes smoothly to zero as $\omega \rightarrow 0$.

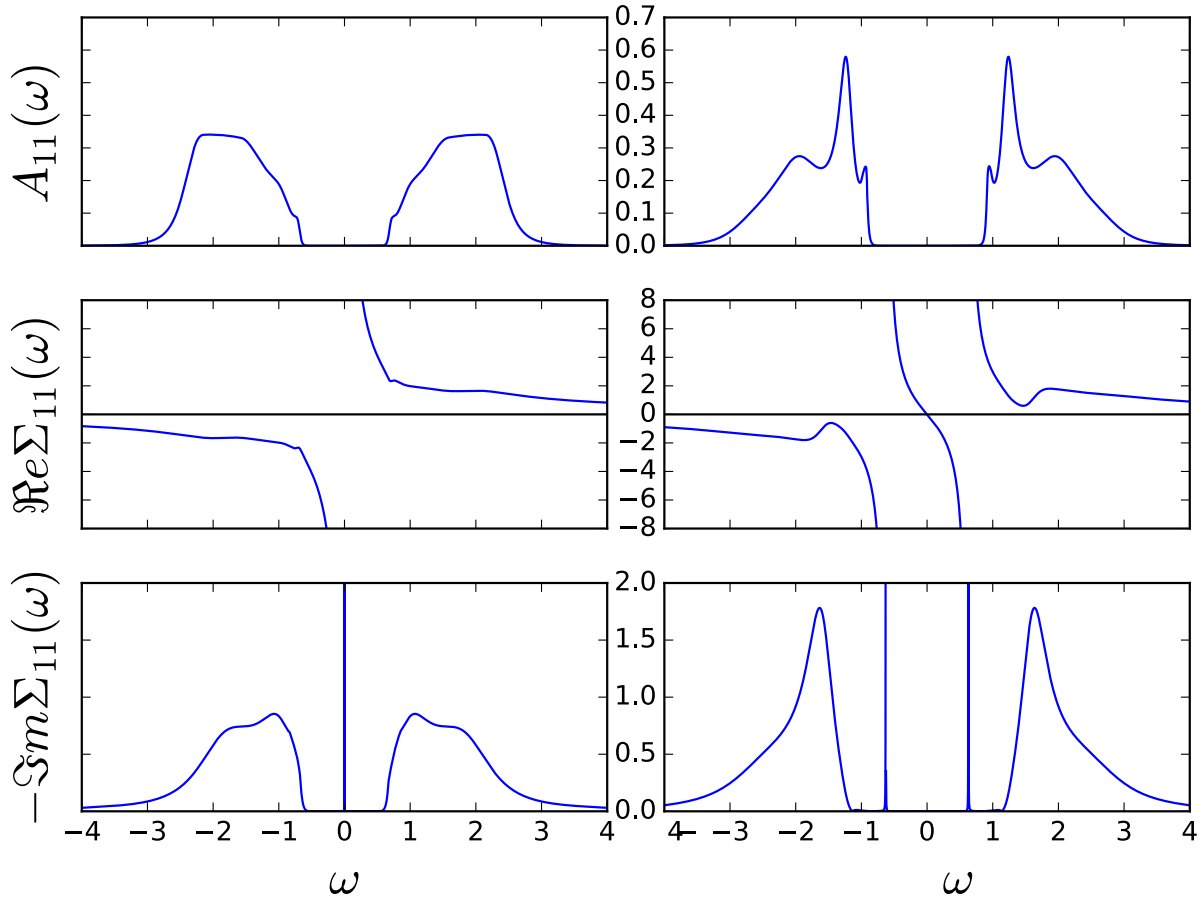


Figure S6. Local Spectral Function(top Panel), Real Part of the Self-Energy(middle) and minus Imaginary part of the self-energy. Left column corresponds to the known DMFT solution of the single band Hubbard model($t_{\perp} = 0$). The right column corresponds to the dimer lattice at $t_{\perp} = 0.3$. For both figures $U = 3.5$

The electronic structure of the dimer model

The dimer Hubbard Model is not a single band model despite being a single orbital per site system. Since it has two sites (the dimer) in the unit cell, there are two bands. The two sites are related by symmetry thus the two bands are degenerate in the atomic-site representation but are distinct in the bonding/antibonding basis. The physics of the system is independent of the choice of the representation. To further clarify this point we show in figure S7 the DOS from our model calculation from Fig. 3 of the manuscript in the atomic-site basis, along with the bonding and antibonding DOS. The average of the latter two gives the former one (which has degeneracy 2).

ELECTRONIC STRUCTURE OF THE ATOMIC (ISOLATED DIMER) LIMIT OF THE LATTICE MODEL

In order to identify the electronic structure of the insulator state of the model, we obtained the corresponding quantity in the atomic limit, which can be analytically solved in the real frequency axis (the impurity model is an isolated dimer). In this limit the lattice Green's function is obtained as,

$$\mathbf{G}_{lat}^{-1} \approx \begin{bmatrix} \omega - \epsilon & -t_{\perp} \\ -t_{\perp} & \omega - \epsilon \end{bmatrix} - \begin{bmatrix} \Sigma_{11} & \Sigma_{12} \\ \Sigma_{12} & \Sigma_{11} \end{bmatrix}_{dimer} \quad (\text{S1})$$

The electronic structure in this limit is shown in figure S8 at 2 different temperatures. The left panel is at inverse temperature $\beta = 100$, where we see two highly dispersive bands along with two flatter ones. At high temperature

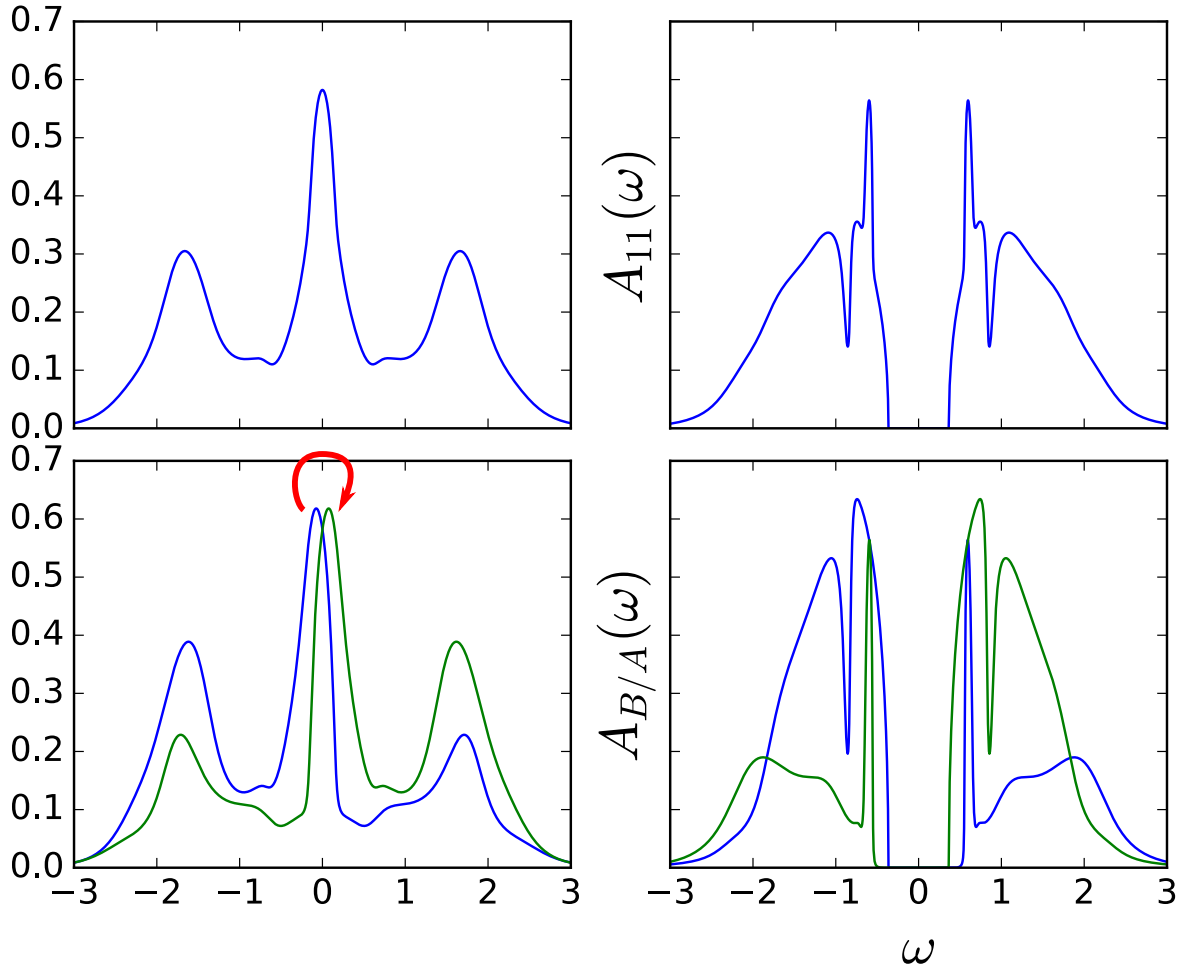


Figure S7. Top panel shows the DOS in the atomic-site basis (from Fig.3 of manuscript) This DOS is doubly degenerate (the same at each of the two atoms of the unit cell). Bottom panel show the DOS in the bonding (blue) and antibonding (green) combinations, respectively. The average of the bottom two DOS gives the top one. Red arrow in bottom left panel indicates the origin of the MIR peak which appears at $\omega \sim 0.22eV$ (cf. fig. S9)

$\beta = 5$ more excitations are apparent as the first excited state of the dimer becomes thermally populated. This dramatically enriches the electronic structure. Interestingly, these multiple excitations can be readily identified in the actual model results shown in the Main Text.

OPTICAL CONDUCTIVITY

To calculate the optical conductivity one requires a geometrical definition of the lattice. As a common practice, one turns to the hypercube in infinite dimensions to keep on with the exact limit of the DMFT approximation [S7]. Using the Peierls ansatz to find the current operator and aligning our dimer along the, say, x direction in the hypercube one finds the current operator along the x direction to be:

$$\hat{j}_x = \sum_{\sigma} e \left[2a \frac{t}{\sqrt{2d}} \sin(k_x a) \left(\hat{b}_{k_x, \sigma}^{\dagger} \hat{b}_{k_x, \sigma} + \hat{a}_{k_x, \sigma}^{\dagger} \hat{a}_{k_x, \sigma} \right) + i\eta t_{\perp} \left(\hat{b}_{k_x, \sigma}^{\dagger} \hat{a}_{k_x, \sigma} - \hat{a}_{k_x, \sigma}^{\dagger} \hat{b}_{k_x, \sigma} \right) \right] \quad (S2)$$

where e is the electron charge, i is the imaginary unit, a is the lattice unit cell length, and $\eta \in (0, a)$ is the separation between atoms of the dimer. When one diagonalizes the lattice Hamiltonian one can see it in terms of quasiparticles that form a bonding (\hat{b}) and an anti-bonding (\hat{a}) band, one uses then the operators $\hat{b}_{k_x, \sigma}^{\dagger}$, ($\hat{b}_{k_x, \sigma}$) to create (annihilate)

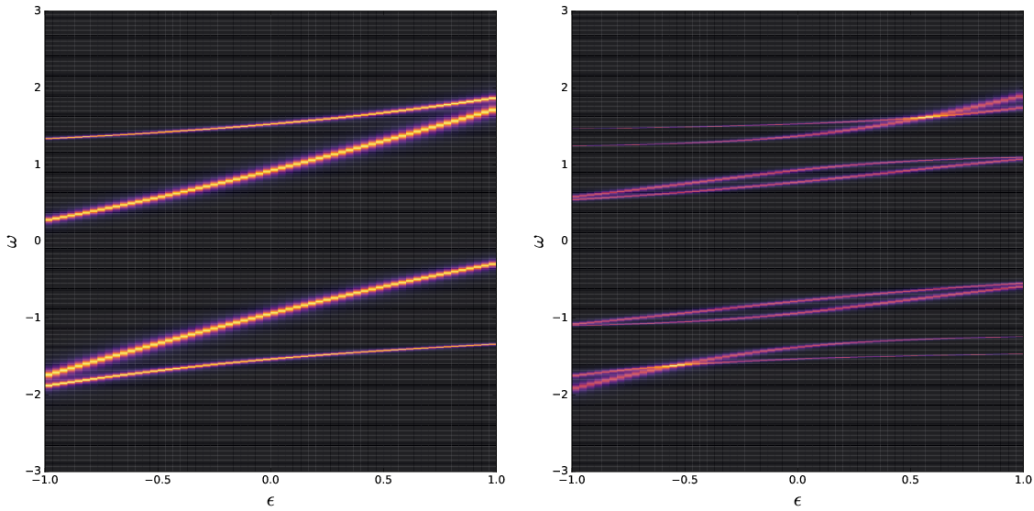


Figure S8. Lattice dispersion approximated with the isolated dimer Self-energy. Setup is ($U = 2.15, t_{\perp} = 0.3$). Left panel at $\beta = 100$ only ground state excitations, right panel $\beta = 5$ presents excitations out of ground state and first excited states.

quasiparticles in the bonding band with momentum k_x and spin σ and analogously the operators $\hat{a}_{k_x, \sigma}^{\dagger}, (\hat{a}_{k_x, \sigma})$ for the anti-bonding band. In infinite dimensions to keep the kinetic energy constant one has to scale the hopping amplitude $t \rightarrow \frac{t}{\sqrt{2d}}$ [S1]. Then following the procedure established in [S7] we arrive to the expression

$$\begin{aligned} \bar{\sigma}_{xx}(\omega) = & \frac{2\pi e^2 a^2 t^2}{d} \int d\omega' \frac{f(\omega') - f(\omega' + \omega)}{\omega} \times \\ & \int dE \rho(E) [A_a(E, \omega) A_a(E, \omega + \omega') + A_b(E, \omega) A_b(E, \omega + \omega')] \\ & + 2\pi e^2 \eta^2 t_{\perp}^2 \int d\omega' \frac{f(\omega') - f(\omega' + \omega)}{\omega} \times \\ & \int dE \rho(E) [A_b(E, \omega) A_a(E, \omega + \omega') + A_a(E, \omega) A_b(E, \omega + \omega')] \end{aligned} \quad (\text{S3})$$

Where $\rho(E) = \frac{\exp(-E^2/(2t^2))}{\sqrt{2\pi t^2}}$ is the density of states of the hypercube, and A_b, A_a are the spectral functions of the bonding and anti-bonding bands. From the previous equation we find that, in general, both intra-band and inter-band transitions are present. Notice that the latter are usually disregarded (e.g. Ref. [S8]). The two contributions are weighted with different factors that depend on the specific geometry. For the sake of simplicity, we set those geometric prefactors equal to unity, as they are expected to be of the same order ($a \sim \eta, t \sim t_{\perp}$ and $d = 3$). In figure S9, we plot for the metal and the insulator case the individual contribution of the interband transitions from the bonding to antibonding bands (refer to figure S7) and of the intraband excitations.

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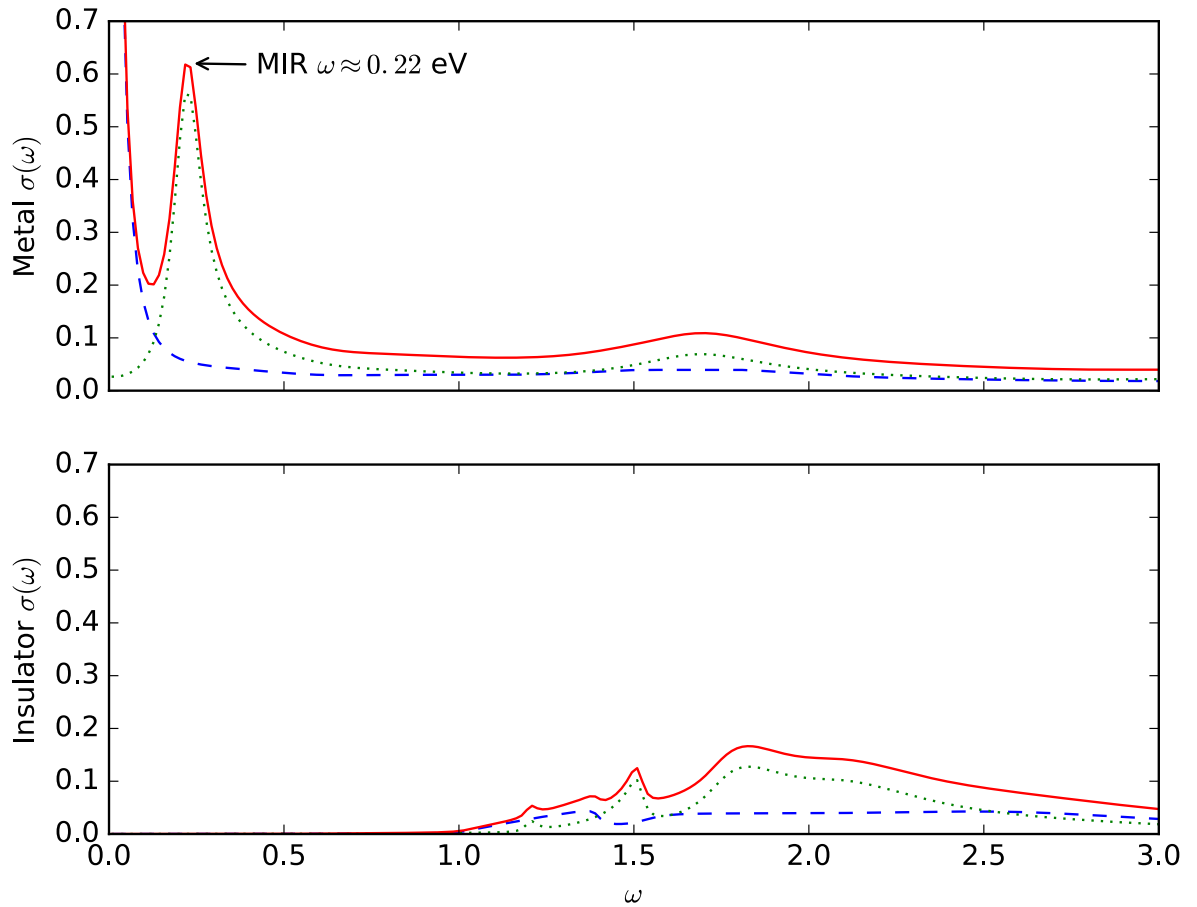


Figure S9. Decomposition of Optical conductivity contributions for metal and insulator. Blue dashed lines are the intraband response, dotted green is the interband excitations, and red is the sum of the two. In the metal there is a MIR peak from interband transitions(cf. figure S7)

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