

***Ab initio* estimate of Hubbard model parameters: A simple procedure applied to BEDT-TTF salts**

Alessandro Fortunelli

Istituto di Chimica Quantistica ed Energetica Molecolare, Consiglio Nazionale delle Ricerche, 56126 Pisa, Italy

Anna Painelli

Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica e Chimica Fisica, Università di Parma, 43100 Parma, Italy

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We describe a simple procedure to extract the parameters of the one-band Hubbard model from a set of *ab initio* calculations on a dimeric unit. The method applies to narrow band solids with negligible orbital relaxation. In this paper we consider a specific system, κ -(BEDT-TTF)₂Cu[N(CN)₂]Br, but the proposed procedure is of general applicability. From a detailed discussion of the *ab initio* data, we extract a few general criteria of wide applicability about the relative magnitude of the empirical model parameters. We prove that the Hubbard model, including both on-site and inter-site electron-electron interactions, is a reliable model for systems with negligible orbital relaxation, apart from particular geometrical arrangements. The hopping parameter (t), as well as the intersite electronic repulsion (V), are barely affected by the chemical environment. On the contrary, the on-site energy and the on-site repulsion (the Hubbard h and U) show an appreciable dependence on the chemical environment, through a dependence of the frontier and core energies on the surrounding potential. [S0163-1829(97)07324-4]

I. INTRODUCTION

The importance of semiempirical models in both molecular and solid-state physics is hardly overemphasized. These models deal with limited basis sets, disregarding high-energy states. Moreover, only a few, hopefully the most important, interactions are accounted for, so that few parameters fully describe the model. Physical intuition is the guide in the choice of the basis set and of the relevant interactions, whereas the parameter values are fixed against experiment. Experiment is also the test of semiempirical models: a valuable model describes the properties of a class of systems in terms of transferable parameters, or in terms of parameters whose variation within the class is easily predictable.

The Pariser-Parr-Pople (PPP) model¹ is one of the simplest and most successful semiempirical models of molecular physics. It describes π electrons in conjugated molecules in terms of electron hopping between adjacent sites, and of site-diagonal electron-electron ($e-e$) interactions, for which a couple of popular parametrizations are available. It is well known that this simple model successfully accounts for the spectroscopic properties of polyenes.² It proved a valuable model also for the spectral properties of π -conjugated polymers,³ as well as for e -ph coupling in *trans*-polyacetylene.⁴

The Hubbard model (HM) is the solid-state counterpart of PPP. The simple HM, which accounts only for on-site $e-e$ interactions, was originally developed to describe d and f electrons in transition metals and oxides,⁵ but was early applied to different classes of systems, like charge transfer salts.⁶ Intersite $e-e$ interactions were later included in the extended Hubbard model.⁷ At present HM is very popular. It is the simplest model describing correlated electrons, and therefore represents the model of choice to describe systems

where $e-e$ interactions play a relevant role. It is currently applied to heavy fermion systems,⁸ conjugated polymers,³ organic charge-transfer salts,^{6,7} and is one of the favorite models to discuss exotic superconductivity in cuprates,⁹ fullerenes,¹⁰ and in organic charge-transfer salts.¹¹

In the field of molecular physics the validity of the PPP model has been formally discussed from a theoretical point of view.¹² On the other hand, the applicability of HM to solid-state systems is still controversial. In recent years, several authors, working in different fields, suggested that additional terms accounting for nonsite-diagonal $e-e$ interactions have to be considered.¹²⁻¹⁸ More generally the approximations underlying the model need to be tested. On the other hand, the estimate of the model parameters is still problematic. Fixing parameters against experiment is difficult due to the variety of systems at hand and of their physical properties.

Recently we have proposed a simple procedure to estimate the HM parameters from the analysis of *ab initio* calculations performed on dimeric units with different charges.¹⁹ The procedure is based on two fundamental assumptions, which constitute the basis of applicability of the HM itself: (a) an adequate description of the physics of the system is possible by accounting for only one orbital per site, and (b) the shape of the orbital is independent of the electronic occupation, i.e., the orbital relaxation (the variation in the shape of the site orbital with the charge residing on it) is negligible. The validity of both assumptions can be verified *a posteriori*. However, we observe that, if the monomer units residing on each site bear a negative charge, the valence orbital is very diffuse and its shape is strongly affected by the electronic occupation. On the contrary the orbital relaxation is minor for monomers bearing positive or null charges.

The proposed procedure, based on the analysis of *ab initio* results on dimeric units, relates the model parameters to

structural and chemical data. The applicability of HM can therefore be discussed for each system at hand and the corresponding microscopic parameters can be reliably estimated. A few general criteria of wide applicability are extracted from this analysis, concerning the relative magnitude of the model parameters as well as their dependence on chemical environment and/or physical structure.

In the present paper we summarize the results of our analysis as applied to κ -(BEDT-TTF)₂Cu[N(CN)₂]Br, a prototype organic superconductor.²⁰ κ -phase BEDT-TTF salts are a fascinating class of systems, and represent an interesting opportunity to test our approach. The physics of these systems is not well understood. In spite of having similar structures, with two-dimensional planes of BEDT-TTF molecules alternating with counter-anion layers, the properties of these systems are variegated: in the same family are present insulators, metals, and superconductors.^{11,20} As a typical example, the three compounds with formula κ -(BEDT-TTF)₂Cu[N(CN)₂]X, and X=Cl, Br, I, are isostructural, nevertheless their properties are remarkably different.^{21,22} The Br compound shows superconductivity at ambient pressure with $T_c = 11.6$ K. The Cl compound has the highest T_c (12.8 K) between organic superconductors, but a small external pressure (0.3 kbar) is required to achieve superconductivity. The I compound does not show superconducting phases. The absence of superconductivity in the I compound has been ascribed to the presence of disorder,²² but the different behavior of the Cl and Br compounds is not understood. In BEDT-TTF salts superconductivity is extremely sensitive to disorder and pressure. Whereas e - e interactions are certainly important in these narrow-band systems, the extreme sensitivity to external perturbations suggests a subtle interplay between competing interactions. In order to understand similarities and differences among compounds of the same class, the empirical model parameters must be carefully tuned. Extended Hückel theory (EHT) has often been used to estimate the hopping integral (the t parameter of the HM or of the tight-binding model) for charge-transfer salts.^{23–26} EHT is mono-electronic and gives no information on e - e interactions. In a pioneering work Ratner, Sabin, and Ball²⁷ estimated both t and the effective on-site e - e repulsion (U) from semiempirical INDO (intermediate neglect of differential overlap) calculations performed on monomeric and dimeric tetracyanoquinodimethane units. More recently, estimates of U and V (the intersite e - e repulsion) have been reported based on CNDO/2 and AM1 semiempirical calculations performed on the isolated BEDT-TTF molecule, or on small clusters.²⁸

We estimate the HM parameters from a detailed analysis of *ab initio* calculations on isolated dimeric units.²⁹ The resulting values are very accurate and allow us to discuss the applicability of HM and the physics governing the magnitude of its parameters. The analysis is carried out on a specific system, κ -(BEDT-TTF)₂Cu[N(CN)₂]Br, but is of general applicability. Indeed, from the discussion of the *ab initio* data we extract a few guidelines of very wide applicability.

The paper is organized as follows. In Sec. II we review the basic features of the empirical model and of the *ab initio* calculations. In Sec. III we analyze the numerical results on κ -(BEDT-TTF)₂Cu[N(CN)₂]Br. We prove that the extended HM, including both on-site and intersite e - e interactions, is a

TABLE I. Energy eigenvalues (\bar{E}_i^Q) for a dimeric unit described by the empirical Hamiltonian of Eq. (1).

$Q=0$	$\bar{E}_1^0 = 4h + 2U + 4V - 2W$
$Q=1$	$\bar{E}_1^1 = 3h + U + 2V - W - (t - 2X)$ $\bar{E}_2^1 = 3h + U + 2V - W + (t - 2X)$
$Q=2$	$\bar{E}_1^2 = 2h + V + W + \frac{U - V - \sqrt{(U - V)^2 + 16(t - X)^2}}{2}$ $\bar{E}_2^2 = 2h + U - W$ $\bar{E}_3^2 = 2h + V + W + \frac{U - V + \sqrt{(U - V)^2 + 16(t - X)^2}}{2}$ $\bar{E}_4^2 = 2h + V - W$
$Q=3$	$\bar{E}_1^3 = h - t$ $\bar{E}_2^3 = h + t$
$Q=4$	$\bar{E}_1^4 = 0$

reliable model. We show that the hopping parameters, which of course depend on the local dimer geometry, are largely independent of the chemical environment and of the charge (no orbital relaxation). Our major result is instead an appreciable dependence of the on-site e - e interaction U on the chemical environment, through a dependence of the frontier and core energies on the surrounding potential. In Sec. IV we discuss the implications of our results for the family of κ -phase BEDT-TTF salts. Finally, in Sec. V we generalize our discussion in order to get some guidelines of general applicability for the estimate of the empirical model parameters.

II. THE EMPIRICAL AND *AB INITIO* MODELS FOR THE ISOLATED DIMER

We consider the most general form of an empirical two-electron model Hamiltonian for a one-band dimer with no orbital relaxation:

$$\begin{aligned}
 \hat{\mathcal{H}}_{\text{EM}} = & h \sum_{\sigma} (n_{1,\sigma} + n_{2,\sigma}) - t \sum_{\sigma} (a_{1,\sigma}^{\dagger} a_{2,\sigma} + a_{2,\sigma}^{\dagger} a_{1,\sigma}) \\
 & + U (n_{1,\alpha} n_{1,\beta} + n_{2,\alpha} n_{2,\beta}) + V \sum_{\sigma,\sigma'} n_{1,\sigma} n_{2,\sigma'} \\
 & + X \sum_{\sigma} (a_{1,\sigma}^{\dagger} a_{2,\sigma} + a_{2,\sigma}^{\dagger} a_{1,\sigma}) (n_{1,-\sigma} + n_{2,-\sigma}) \\
 & + \frac{W}{2} \sum_{\sigma} (a_{1,\sigma}^{\dagger} a_{1,-\sigma} a_{2,-\sigma} a_{2,\sigma} + a_{2,\sigma}^{\dagger} a_{2,-\sigma} a_{1,-\sigma} a_{1,\sigma}) \\
 & + \frac{W}{2} \sum_{\sigma,\sigma'} (a_{1,\sigma}^{\dagger} a_{2,\sigma'} a_{1,\sigma'} a_{2,\sigma} + a_{2,\sigma}^{\dagger} a_{1,\sigma'} a_{2,\sigma'} a_{1,\sigma}),
 \end{aligned} \tag{1}$$

where $\sigma = \alpha, \beta$ is the spin variable, $n_{i,\sigma} = a_{i,\sigma}^{\dagger} a_{i,\sigma}$, and $a_{i,\sigma}^{\dagger}$ ($a_{i,\sigma}$) is the creation (annihilation) operator for the orbital centered on site i with spin σ . This Hamiltonian conserves the total charge on the dimer, $Q = 4 - n$, where n is the total

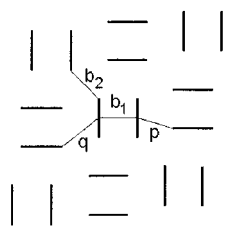


FIG. 1. Schematic projection view of a BEDT-TTF layer. The long molecular axis lies in the direction perpendicular to the drawing plane. All molecules are equivalent. Letters indicate the four interactions considered in the text.

number of electrons. Therefore it can be exactly diagonalized for each Q value. The analytical expressions for the eigenvalues (\bar{E}_i^Q) are reported in Table I. From Table I it is apparent that the estimate of the parameters of the empirical model requires the ground-state energies and the first-excitation energies of isolated dimers bearing charges ranging from 0 to 4. This information is in general not experimentally available. Therefore we resort to first-principle quantum chemistry calculations on isolated BEDT-TTF dimers. We need a large set of dimer energies since we want estimate all the parameters of the general Hamiltonian in Eq. (1), in order to assess the reliability of simpler models like the HM. On the contrary if one wants to estimate the few parameters relevant to the simple HM, a limited set of monomer and/or dimer energies is required. For example, as originally recognized in the parametrization of the PPP model,¹ U can be obtained from the difference between the ionization potential and the electronic affinity of the isolated orbital. Analogously, only two dimeric energies are enough to estimate t , thus getting a complete parameter set for the simple Hubbard model.^{1,12,23–27}

κ -(BEDT-TTF)₂Cu[N(CN)₂]Br crystallizes in the orthorhombic space group $Pnma$, with BEDT-TTF molecules residing on equivalent sites. The basic structural unit is a pair of faced molecules with nearly parallel molecular planes. The pairs arrange themselves nearly perpendicularly in a checkboard pattern to construct a bidimensional sheet, as sketched in Fig. 1. These donor sheets are intercalated by anion sheets. EHT calculations predict that nonnegligible interactions occur along the directions b_1 , p , q , and b_2 , as indicated in Fig. 1. We have singled out the corresponding four dimeric units, and have performed *ab initio* calculations on them.

For each dimer we used the experimental geometry at 120 K,²² setting standard tetrahedral C-H bonds for the ethylenic groups. We use GAUSSIAN 94 programs,³⁰ adopting a 6-31G** basis set, to calculate the ground state energies for the various Q , as well as the triplet energy for $Q=2$, in the restricted Hartree-Fock scheme (RHF-SCF). The energies of the lowest singlet states for $Q=2$ are calculated at the complete active space (CAS-SCF) level. The *ab initio* energies, \bar{E}_i^Q , are reported in Table II. The table is not complete since unfortunately we were not able to converge to the RHF ground state for the $Q=3$ dimers, nor to the CAS-SCF solutions for the excited singlet states at $Q=2$.

Additional information is obtained by performing frozen orbital calculations. In fact, an independent estimate of the

parameters of the empirical model can be obtained by evaluating the matrix elements of the *ab initio* Hamiltonian on the basis of local orbitals.¹⁹ As an example, $\langle \varphi_1 | \hat{h} | \varphi_1 \rangle$ is the *ab initio* matrix element corresponding to the on-site energy of the valence orbital localized on the 1 site, and so on. Therefore, for each dimer we localized the RHF-SCF orbitals obtained at different fixed total charge and computed the following *ab initio* matrix elements: $h = \frac{1}{2}(h_{11} + h_{22})$, $\Delta h = \frac{1}{2}(h_{22} - h_{11})$ (h_{ii} representing the on-site energy of the i th site); t (the hopping integral); $U = \frac{1}{2}(U_1 + U_2)$, $\Delta U = \frac{1}{2}(U_2 - U_1)$ (U_i representing the on-site $e-e$ repulsion); V (the repulsion between charges on adjacent sites); W (the self-repulsion of the bond charge); X (the repulsion between site and bond charges; in the local orbital basis $X = X_1 = X_2$ ¹⁹). In Table III we summarize the results obtained in the four geometries using the RHF-SCF orbitals calculated with $Q=0, 2$, and 4.

III. ANALYSIS OF THE RESULTS

Symmetric vs asymmetric dimers

The empirical Hamiltonian in Eq. (1) is written in the hypothesis that the two monomers are equivalent in the dimer. This is the obvious choice in modeling crystals with equivalent (or nearly equivalent) sites. In this case the on-site parameters h and U are the same for the two monomers so that the total number of parameters is smaller than the number of independent *ab initio* energies. The analysis of the results is therefore direct. However, even in crystals made up of equivalent sites, one can single out a nonsymmetric dimer. In our case, as it is apparent from Fig. 1, b_1 and b_2 dimers are symmetric, whereas p and q are not. For nonsymmetric dimers, finite Δh and ΔU values lead to rather involved equations for the *ab initio* energies.¹⁹ Moreover, the number of parameters is larger than the number of independent *ab initio* energies. In this case, to estimate all the model parameters one must use results from an independent set of calculations, like the frozen-orbital calculations.

Indeed, even in the case of b_1 and b_2 symmetric dimers, due to the lack of convergence of RHF-SCF calculations for the ground state at $Q=3$ and of CAS-SCF for the two excited singlets at $Q=2$, we cannot extract from the SCF energies all the parameters of the empirical model, so that frozen orbital calculations have been used for symmetric dimers, too.

The hopping integrals and non-site-diagonal parameters

The eigenvalue expressions in Table I suggest that the hopping parameters can be estimated from the energy difference between the ground and the first excited state for the dimers with $Q=1$ and 3: $t - 2X = (\bar{E}_2^1 - \bar{E}_1^1)/2$; $t = (\bar{E}_2^3 - \bar{E}_1^3)/2$. Equivalently we can estimate $t - 2X$ as the difference between the ionization potentials of the ground and the first excited state with $Q=0$. According to the Koopmans's theorem the ionization potentials are equal to the orbital energies (ϵ^0), so that $t - 2X = -\frac{1}{2}[\epsilon^0(\text{HOMO}) - \epsilon^0(\text{HOMO} - 1)]$. Analogously, we estimate t as a difference between electron affinities: $t = -\frac{1}{2}[\epsilon^4(\text{LUMO} + 1) - \epsilon^4(\text{LUMO})]$. These t and X estimates are reliable, in fact they are obtained

TABLE II. Results of RHF-SCF and CAS-SCF calculations on BEDT-TTF dimers. The symbols for the energies (\tilde{E}_i^0) and the orbital eigenvalues (ϵ^0) are explained in the text. The state energies (a.u.) are measured with respect to the energy -7125 a.u.; the orbital eigenvalues are in eV.

geo	\tilde{E}_1^0	ϵ^0 HOMO-1	ϵ^0 HOMO	\tilde{E}_1^1	\tilde{E}_1^2	\tilde{E}_4^2	\tilde{E}_1^4	ϵ^4 LUMO	ϵ^4 LUMO+1
b_1	-1.549 44	-6.66	-6.12	-1.344 48	-1.048 90	-1.045 63	-0.046 11	-14.24	-13.70
p	-1.561 08	-6.56	-6.31	-1.356 00	-1.068 36	-1.067 83	-0.097 42	-13.54	-13.26
q	-1.568 30	-6.50	-6.42	-1.361 92	-1.079 27	-1.079 28	-0.129 45	-13.10	-12.99
b_2	-1.566 84	-6.51	-6.35	-1.349 16	-1.081 42	-1.081 21	-0.132 32	-13.14	-12.97

from differences of orbital energies, which, in systems with negligible orbital relaxation, are rather insensitive to the chemical environment and to electron correlation.

From the data in Table II we get $t_{b_1}=0.272$ eV, $X_{b_1}=0.003$ eV, $t_{b_2}=0.085$ eV, $X_{b_2}=0.0025$ eV. These values are in striking agreement with the frozen orbital results in Table III, which, in turn, are nearly independent of Q . This invariance of the t estimates confirms that orbital relaxation is irrelevant in BEDT-TTF salts, in agreement with physical intuition. In fact orbital relaxation is expected to be more effective the more negative the oxidation state of the involved species is, whereas BEDT-TTF molecules bear positive or null charges. The negligible role of orbital relaxation is further confirmed by the smallness of X . The equivalence of SCF and frozen orbital estimates of t and X for the symmetric dimers makes us confident in using frozen orbital t and X estimates in the case of asymmetric dimers. By averaging the values in Table III we get $t_p=0.13$ eV, $X_p=0.003$ eV, $t_q=0.04$ eV, $X_p=0.004$ eV.

We further notice that even in the b_1 geometry, where intermolecular interactions are the largest, the differences $\frac{1}{2}[\epsilon^4(\text{LUMO}+3)-\epsilon^4(\text{LUMO}+2)]=0.005$ eV and $\frac{1}{2}[\epsilon^4(\text{HOMO}-2)-\epsilon^4(\text{HOMO}-3)]=0.022$ eV are small. These energy differences are related to the hopping integrals for *inner* valence orbitals. They are much smaller than t or $t-2X$, strongly supporting *one band* models.

W , an intersite parameter, corresponds to a *diagonal* matrix element. As such, it has to be contrasted with $4t^2/(U$

$-V)$ rather than with t (as often done). Due to the lack of convergence of the CAS-SCF excited-state calculations at $Q=2$, W is estimated from frozen orbitals results. These calculations show that W is negligible (see Table III), except at the q geometry, where $W\sim 4t^2/(U-V)$. This result can be related to the special geometry of the orbital interaction at the q geometry (see below). The q dimer thus provides an interesting example of a system where $X\ll t$ but $W\sim 4t^2/(U-V)$, so that ferromagnetic interactions are stabilized, as proved by the triplet state having a slightly lower energy than the singlet state at $Q=2$ ($\tilde{E}_4^2<\tilde{E}_1^2$, see Table II). However, the interactions estimated in the q geometry are weaker than those relevant to other geometries, so that the relative importance of W in the crystal is small.

In summary, for the system at hand nonsite-diagonal $e-e$ interactions, as measured by X and W terms, are negligible and the standard extended HM is applicable.

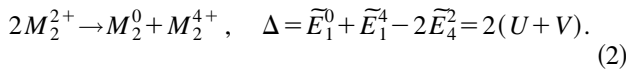
The site-diagonal parameters

The frozen orbital results in Table III show that for all geometries V is nearly independent of Q . V represents the interaction between two poorly overlapping charge distributions and, as such, barely depends on the orbital shape. We estimate V as the average of $Q=0$ and $Q=2$ frozen orbital results, as follows: $V=3.18, 2.45, 2.14,$ and 2.09 eV for the $b_1, p, q,$ and b_2 geometries, respectively. V smoothly decreases as the two monomers get apart.

TABLE III. *Ab initio* parameters (eV) for localized frozen orbitals derived from RHF-SCF calculations at the $b_1, p, q,$ and b_2 geometries with total charge $Q=0, 2, 4$.

geo	Q	h	Δh	t	U	V	ΔU	W	X
b_1	4	-13.97	0	0.272	5.44	2.83	0	0.0035	-0.0046
b_1	2	-16.84	0	0.279	6.40	3.26	0	0.0051	0.0192
b_1	0	-18.24	0	0.301	5.58	3.14	0	0.0052	0.0174
p	4	-13.40	-0.0516	0.129	5.49	2.32	-0.0014	0.0011	0.0037
p	2	-15.78	-0.0302	0.122	6.48	2.46	0.0092	0.0010	0.0020
p	0	-16.90	0.0002	0.135	5.57	2.45	-0.0057	0.0024	0.0030
q	4	-13.05	0.0463	0.034	5.53	1.96	-0.0034	0.0014	0.0035
q	2	-15.27	0.0286	0.037	6.49	2.11	-0.0002	0.0006	0.0039
q	0	-16.33	0.0170	0.047	5.55	2.16	-0.0016	0.0036	0.0036
b_2	4	-13.06	0	0.085	5.55	2.04	0	0.0013	0.0001
b_2	2	-15.25	0	0.082	6.52	2.09	0	0.0001	0.0010
b_2	0	-16.23	0	0.080	5.58	2.09	0	0.0021	-0.0032

Frozen orbital U and h values appreciably depend on Q . As extensively discussed in Ref. 19, the frozen orbital U value corresponds to the self-interaction of an on-site charge distribution and therefore is very sensitive to the detailed form of the orbitals. Moreover, the proper estimate of the effective U value corresponds to a difference between ionization potential and electron affinity of the $Q=1$ site,¹ which strongly depends on the energy relaxation of both valence and core orbitals. We can estimate the effective U value from the calculated SCF energies, using the following disproportionation reaction involving dimeric units (M_2):



Adopting the frozen orbital estimate estimate for V , we get $U = 3.56, 4.04, 4.13,$ and 4.21 eV, for $b_1, p, q,$ and b_2 geometries, respectively. The SCF U estimates differ appreciably from the frozen orbital values in Table III. This is due to the *energy* relaxation. In fact, in frozen orbital calculations we do not allow valence nor core orbitals to relax in order to accommodate an increasing number of electrons. Therefore, the SCF values of both \bar{E}_1^0 and \bar{E}_1^4 are lower than the corresponding energies calculated with the frozen orbitals relevant to the $Q=2$ dimer. Of course, the physically relevant U value corresponds to the SCF estimate.

A second important observation is that U , which is in general regarded as a molecular property, actually depends on the dimer geometry, or, equivalently, on the potential experienced by the on-site orbitals. The U value is affected by the ‘‘chemical environment’’ since U must account for the energy relaxation of core and valence orbitals and therefore contains a contribution from the potential that the orbitals experience.¹⁹ In fact, as the monomers get apart, the dimer U value converges to the isolated monomer value, $U = 4.48$ eV, as estimated from the following disproportionation reaction involving a monomer unit (M):



The on-site energy h can be estimated as $h = (\bar{E}_4^2 - \bar{E}_1^4 - V + W)/2$, with $V - W$ taken from frozen orbital calculations. The resulting values are $h = -15.19, -14.43, -13.99,$ and -13.96 eV, for $b_1, p, q,$ and b_2 geometries. Once again we find an appreciable dependence on the geometrical arrangement.

IV. DISCUSSION

For the sake of comparison we have performed EHT calculations³¹ on the four dimers of interest, and have evaluated the corresponding t from the splitting of the frontier orbitals.²³ We get $t = 0.22, 0.094, 0.040,$ and 0.071 eV for $b_1, p, q,$ and b_2 geometries, respectively. These values compares well with our SCF results, confirming that EHT gives good estimates of hopping integrals, at least in systems where the orbital relaxation is negligible and X and W are small. In κ -(BEDT-TTF)₂Cu(NCS)₂, a system very similar to the one we consider in this paper, the EHT band structure well reproduces the experimental data,³² and is in good agreement with the band structure calculated through extensive first-principle calculations.³³ Therefore the matching be-

tween our *ab initio* estimates and the EHT values makes us confident in a reasonable agreement with experiment. On the other hand, t estimates from *ab initio* calculations performed with the STO-3G basis set largely deviates from both 6-31G** *ab initio* and EHT results, with $t = 0.100, 0.146, 0.071,$ and 0.031 eV, for the b_1, p, q and b_2 geometries, respectively. It is known that the 6-31G** basis we adopted for *ab initio* calculations represents the best compromise between accuracy and CPU time.

Due to the appreciable dependence of U on the chemical environment, the estimate of U from dimer calculations is problematic. However, the value relevant to b_1 dimer, $U \sim 3.56$ eV, can be taken as our best estimate. This value compares reasonably with the AM1 estimate (3.90 eV) for a monomer in the β -(BEDT-TTF)₂I₃ crystal.²⁸ Comparing this quantity with experimental data is not obvious. The experimental effective U in fact represents a balance of on-site and intersite (also long-range) *e-e* interactions. Our estimate of the effective *e-e* interactions in the isolated b_1 dimer, $U - V \sim 0.4$ eV, compares favorably with the available experimental estimates for the κ -phase BEDT-TTF crystals, ranging from 0.4 to 0.7 eV.³⁴⁻³⁶ More stringent tests can be obtained from the comparison with the optical spectra of crystals where isolated, or nearly isolated BEDT-TTF dimers are present. Preliminary experimental data on the (BEDT-TTF)₂Mo₆O₁₉ indicate that our estimates are in the correct range.³⁷

Our *ab initio* estimate of the Hubbard model parameters compares well with semiempirical estimates, as well as with the few available experimental estimates of the microscopic parameters. This makes us confident in the overall reliability of the proposed procedure. Whereas the comparison of our results with the spectral properties of an isolated BEDT-TTF dimer would confirm our energy calculations, a thorough test of the reliability of our parameter set would imply the comparison with true solid state properties. This comparison is not at all trivial: when our parameter set is put into the Hamiltonian describing the solid, we end up with a problem of interacting electrons (the two-dimensional extended Hubbard model).

Even if in the (BEDT-TTF)₂Cu(NCS)₂ crystal the EHT band structure reproduces the details of the Fermi surface as extracted from experiment,³² there are many evidences that a single-electron picture cannot explain the general behavior of the κ -phase BEDT-TTF salts. κ -(BEDT-TTF)₂Cu[N(CN)₂]Br is isostructural with the Cl analog.²² For the Cl compound we have performed EHT calculations³¹ on the four dimers of interest, and calculated $t = 0.23, 0.090, 0.041,$ and 0.076 eV for the $b_1, p, q,$ and b_2 geometries, respectively. These values are practically coincident with the EHT values obtained for the Br-analogue. In fact extensive EHT band calculations on the κ -(BEDT-TTF)₂Cu[N(CN)₂]X family give strikingly similar band structures,²² in spite of the very different physical properties of the three crystals. On the other hand, U is usually considered a molecular parameter independent of the environment. In this view, the different behavior of the Cl and Br compounds (we do not discuss the I compound due to the possible role of disorder) cannot be rationalized at all in the frame of the HM. Often different crystal properties, and particularly different phonon structures are supposed to make

the difference between the two compounds through subtle interactions between the cation and the anion layers.^{22,38} Here we suggest a different possibility: U is strongly affected by the chemical environment, therefore the U values relevant to the three compounds need not to be the same, differences of the order of (or even greater than) 20% being expected. Calculations are in progress to verify this prediction.

A second indication that single-electron models as well as standard parametrizations of the Hubbard model are inadequate is offered by the study of (BEDT-TTF)₂Cu(NCS)₂ under pressure. Based on crystallographic data collected under pressure, EHT band-structure calculations predict, for this salt, a reduction of the size of the closed orbits on the Fermi surface.³⁹ On the contrary Shubnikov–de Haas oscillations unambiguously indicate that the area increases by about 30%, in going from ambient pressure up to 16.3 kbar.³⁵ In our view, the large environment effect on U implies a non-negligible pressure dependence of U . Since in these systems small U variations can originate large effects,⁴⁰ we believe that the environment dependence of U must not be disregarded.

V. CONCLUSIONS

In the present paper we have discussed a general procedure to extract the empirical model parameters from *ab initio* calculations on dimeric units. Since all parameters are extracted from a single set of calculations we get reliable estimates of the relative magnitude of the parameters. Therefore the validity of the various approximations underlying the empirical model can be easily tested.

The proposed procedure has been applied to a specific system, κ -(BEDT-TTF)₂Cu[N(CN)₂]Br, a typical representative of the organic superconductors. For this system we showed that bond-site and bond-bond charge repulsion terms (X and W , respectively) are negligible, and the standard extended HM is therefore applicable. However in the standard approach U and h are considered “molecular” or “site” parameters, and as such are assumed independent of the geometrical arrangement and/or chemical environment. Instead we find large variations of these parameters with geometry. In the previous section we suggested that some of the peculiar properties of the BEDT-TTF salts of the κ -phase family could be ascribed to the considerable dependence of U on geometry and chemical environment.

Here we generalize the discussion with the aim of extracting information of wider applicability. It is well known that, in systems where orbital relaxation is important, finite and possibly large X values can be found.^{15–18} Instead our calculations proved that, for the system at hand, the standard Hubbard model, with no interaction terms involving bond charges, is applicable. We believe this is a *general result* for systems with no orbital relaxation. The Hubbard model is defined in terms of mutually orthogonal *local* orbitals centered on the sites. The Mulliken approximation applied to the calculation of relevant integrals then leads to negligible X and W values.¹⁴ The applicability of the Mulliken approximation is questionable for nearest-neighbor sites. However in Ref. 19 we have shown that X and W stay negligible if calculated for a model dimer with s -type Gaussian site orbit-

als. An older analysis¹⁴ based on p -type Slater orbitals and δ -function interaction suggests that this result is general.

Large deviations from the Mulliken approximation, and therefore non-negligible X and W terms, can instead be predicted when, due to special geometrical arrangements, the overlap integral between the two site orbitals differs appreciably from the overlap integral of their moduli. In Ref. 19 we discussed, as an extreme model example, the case of two orbitals p_x and p_y interacting along the z direction. Due to symmetry, the overlap between the two orbitals vanishes, as well as t and X , but a finite W interaction is calculated. In intermediate cases, in which p_y goes into a linear combination of p_x and p_y , finite and comparable t , X , and W values can be obtained.¹⁹ It would be very interesting to investigate experimental systems, where, due to special geometrical arrangements of this kind, ferromagnetic interactions are favored. Indeed, the q dimer discussed in Sec. III represents a first example of this kind.

Having established that the standard extended HM is usually applicable to systems where orbital relaxation is not important, with some caveats only for systems with special orbital orientations, we now discuss the Hubbard model parameters. The Hubbard U is in general considered a site parameter, independent of chemical environment and of physical variables like pressure. The large difference between SCF and frozen-orbital U estimates, as well as the large variation of U with the dimer geometry, suggest instead a definite sensitivity to the environment. This is a general result: U measures the differential energy required to put two electrons in the same site orbital, therefore it also accounts for the variation with the total charge of the energy of all (valence and core) site orbitals. This total energy relaxation amounts to a fairly large quantity and depends on the potential the orbitals do experience. This is the main reason for the U dependence on the external potential. A similar discussion holds true for the on-site energy h .

The t estimate from *ab initio* calculations is very easy. In systems with negligible orbital relaxation (i.e., in systems where frozen-orbital and SCF t estimates coincide) the t values are barely affected by electron correlations and by the chemical environment, as proved by the general analysis in Ref. 19. Reliable t values can thus be obtained from the RHF-SCF orbital energies relevant to closed shell dimers with 0 and 4 electrons. Similarly V , the intersite e - e interaction, is insensitive to environment, and its frozen-orbital estimates are accurate.

The procedure we propose to extract empirical model parameters from *ab initio* calculations on a dimeric unit accounts for a single relevant orbital on each monomer site and assumes that the orbital itself does not depend on the total charge on the dimer. Apart from these two assumptions that can be verified *a posteriori*, the procedure focuses on an isolated dimer and neglects all the interactions with the surrounding crystal. It is not difficult, in principle, to account for the “static” interactions, in terms of a mean potential due to the rest of the crystal. As discussed at length in the previous two sections this correction will appreciably affect only U and h estimates. “Dynamic” interactions involving screening effects due to the rest of the crystal can be included into the *ab initio* procedure, for example, through the approach proposed in Ref. 41.

Of course the proposed procedure suffers the same limitations as the adopted *ab initio* calculations. HF-SCF calculations include *e-e* interactions in a mean-field-type approximation, so that the electronic correlation is neglected. In recent years, in the field of molecular physics, Freed and co-workers¹² developed a rigorous strategy to extract the empirical model parameters from *ab initio* calculation properly accounting for correlation effects. The procedure is, however, extremely heavy from a computational point of view, and at present is limited to very small systems (the most recent applications concern the benzene molecule). Instead our approach is rather inexpensive and can be applied to systems of interest for solid-state physics. Furthermore, the procedure can be easily generalized to include short-range correlation effects through an approximate version of the

density-functional theory. The effects of both short-range correlations and of the static external potential should be included if very precise *U* and *h* estimates are required. On the contrary, long-range correlations are expected not to be important in systems, like charge transfer salts, where they cannot propagate through an extended σ backbone, as happens, e.g., in conjugated polymers.

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