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Valence Bond Theory of Organic Charge-Transfer Salts†

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A valence bond (*VB*) description is introduced for organic charge-transfer (*CT*) salts based on mixed stacks $\ldots D^{+\gamma}A^{-\gamma}D^{+\gamma}A^{-\gamma}\ldots$ of donors (*D*) and acceptors (*A*). Extrapolating exact results for finite rings shows that the magnetic gap ΔE_m is finite for $\gamma < \gamma_c = 0.68 \pm 0.01$ and vanishes for $\gamma > \gamma_c$ as expected in the paramagnetic ionic limit $\gamma = 1$. The small finite ΔE_m in the "ionic" TMPD-TCNQ complex indicates incomplete *CT*, in agreement with the resonant Raman result of $\gamma \sim 0.7$. The extension of diagrammatic *VB* techniques to partly-filled segregated ion-radical stacks like $\ldots A^{-\gamma}A^{-\gamma}A^{-\gamma}A^{-\gamma}$ or $\ldots D^{+\gamma}D^{+\gamma}D^{+\gamma}D^{+\gamma}\ldots$ is discussed.

I INTRODUCTION

Solid state complexes of organic donors (*D*) and acceptors (*A*) often crystallize in mixed stacks, $\ldots D^{+\gamma}A^{-\gamma}D^{+\gamma}A^{-\gamma}\ldots$, with π-electron overlap and charge-transfer (*CT*) excitations restricted to the stack.[1] A single *CT* integral $t = \langle D^+A^-|\mathscr{H}|DA\rangle$ occurs when *D* and *A* are at inversion centers. In the ground state, the $t \to 0$ limit reduces to $\gamma = 0$ or 1, depending on the balance between the Madelung energy, *M*, of the ionic ($\gamma = 1$) lattice and the cost $I_D - A_A$ of producing a D^+A^- pair.[2] A rapid, but not necessarily discontinuous, change in γ occurs[3] near $M \sim |I_D - A_A|$ for small $|t|$. While most organic *CT* complexes are neutral ($\gamma \sim 0$), strong donors and acceptors form ion-radical solids whose static magnetic susceptibility $\chi(T)$ goes as[1]

$$T\chi(T) \propto \exp(-\Delta E_m/kT) \tag{1}$$

in the region $200 < T < 350$ K. The magnetic gap ΔE_m is of the order of 0.1 ev, or almost as large as the *CT* integral $|t|$. *No* magnetic gap occurs[4] in the regular Heisenberg antiferromagnet (*AF*), to which a regular ionic

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($\gamma = 1$) stack reduces rigorously for $M - (I_D - A_A) \gg |t|$. Resolving the physical origin of such large ΔE_m is consequently the first problem in modelling ionic *CT* complexes.

We have recently introduced[5] a valence-bond (*VB*) analysis of the ground state *CT* $\gamma(z)$ and the magnetic gap $\Delta E_m(z)$ for arbitrary ratios of $z = \delta/\sqrt{2}|t|$, where $\sqrt{2}|t|$ is the *CT* matrix element between $|DA\rangle$ and the singlet[1] $|D^+A^-\rangle$ and -2δ is the excitation energy for $DA \rightarrow D^+A^-$. Quite generally, *VB* methods are preferable in narrow-band (small t) systems, since they reduce correctly to the $t \rightarrow 0$ limit. By contrast, even Hartree–Fock molecular orbital (*MO*) theory, which is clearly a good starting point for large t, incorrectly predicts that H_2 dissociates with equal probability into $H + H$ and $H^+ + H^-$. Of course, configuration interaction (*CI*) in the *MO* approach eventually provides a description of the electron correlation that are built into the *VB* method, but such extensive *CI* is usually prohibitive.

The *VB* model[5] for mixed $\ldots D^{+\gamma}A^{-\gamma}D^{+\gamma}A^{-\gamma}\ldots$ stacks is a natural extension of the *DA* dimer originally discussed by Mulliken.[6] The physical picture of neglecting high-energy D^{+2} and A^{-2} sites, of enumerating all possible *VB* structures, and of treating long-range Coulomb interactions self-consistently are summarized in Section II. The collective nature of long-range, three-dimensional interactions was central to the sharp separation[2] into neutral ($\gamma = 0$) and ionic ($\gamma = 1$) complexes in the nonoverlapping limit $t \rightarrow 0$. Such sharp, first-order transitions are regained as special cases in the more realistic case of $t \neq 0$.

Section III presents experimental evidence based on systematic resonance Raman studies[7] of TCNQ salts. The 1 : 1 complex TMPD-TCNQ of the excellent donor D = NNN′N′-tetramethyl-*p*-phenylenediamine and the excellent acceptor A = tetracyanoquinodimethane is shown to be less than completely ionic, with $\gamma \sim 0.7$, contrary to previous expectations and in agreement with the *VB* result for a *CT* complex with a small magnetic gap of 0.07 ev. The related "ionic" complexes[1] of Chloranil, which is a weaker acceptor than TCNQ, such as TMPD-Chloranil or PD-Chloranil have larger ΔE_m and have even smaller γ. Thus there are no obvious candidates for fully ionic ($\gamma \sim 1$) 1 : 1 *CT* complexes.

A number of extensions of the *VB* method are under consideration. For example, 1 : 1 complexes[8] of substituted phenazines and TCNQ crystallize in mixed alternating stacks, with two transfer integrals t and t'. These *CT* complexes are close to the neutral-ionic interface. A rather more complicated extension is to segregated stacks, especially when there is partial filling with less than one unpaired electron per site. Now only the idea of narrow bands (small t) remains and the *VB* structures, operators, and analysis are quite different. Partially filled segregated stacks encompass all the currently known and intensively studied organic conductors.[9] It is curious that no quantitative analysis of such a static thermodynamic quantity as the magnetic susceptibility $\chi(T)$ is available for *any* organic conductor. We hope that *VB* analysis of partly-filled segregated stacks will remedy the interpretation of $\chi(T)$ data, thereby providing another step in modeling these unusual conductors.

II VALENCE BOND THEORY OF CT COMPLEXES

VB methods were originally introduced[10] in theoretical chemistry as generalizations of the Heitler–London ansatz for bonding in H_2, which corresponds simply to the function

$$\psi(1, 2) = C[1s_A(1)1s_B(2) + 1s_B(1)1s_A(2)](\alpha_1\beta_2 - \beta_1\alpha_2)/\sqrt{2} \tag{2}$$

Here C is a normalization constant, A and B denote the protons, and the singlet spin function of the two electrons 1,2 is associated with the bonding state. Such covalent bonds can be envisioned for other atomic orbitals than $1s$. Drawing a line for each bond, whether σ or π, provides a convenient and powerful representation of organic molecules,[10] even in the case of resonance when no unique *VB* diagram is possible. The great virtue of *VB* methods is their explicit inclusion of electron-electron correlation, since the two electrons in $\psi(1, 2)$ are never on the same proton. On the other hand, *VB* functions[10,11] have inconvenient orthonormalization properties, are difficult to compute with, and usually involve some arbitrary choice based on "chemical intuition." They are consequently far less commonly used in theoretical computations for molecules than various *MO* schemes, although a renaissance is in progress[12] in the use of explicitly correlated wavefunctions.

Mulliken[6] considered the *CI* problem of closed-shell D and A molecules forming a weakly-overlapping DA dimer. The singlet $\psi_{DA}(1, 2)$ has both electrons in the highest-occupied *MO* of D, while the singlet $\psi_{D^+A^-}(1, 2)$ based on Eq. 1 has one electron transferred to the lowest unoccupied *MO* of A (thus producing an A^- ion radical). The singlet ground state wavefunction, neglecting overlap between *MO*s on D and A, is

$$\psi(1, 2) = \cos\phi\,\psi_{AD}(1, 2) + \sin\phi\,\psi_{A^-D^+}(1, 2) \tag{3}$$

where ϕ depends[7b] on the ratio of $-\sqrt{2}|t| = \langle\psi_{D^+A^-}(1, 2)|\mathscr{H}|\psi_{DA}(1, 2)\rangle$ to the energy difference -2δ between $E(D^+A^-)$ and $E(DA)$. When the high-energy $D^{+2}A^{-2}$ singlet is neglected, *CI* between the two singlets depends on the ratio $z = \delta/\sqrt{2}|t|$, while the D^+A^- triplet level is unshifted at $E(D^+A^-)$.

The same approach of assigning electrons to spin-paired D or D^+A^- wavefunctions can be carried out[5] for mixed $\ldots DADA \ldots$ stacks. The principal problem is the enormous number of *VB* structures, which increases faster than 2^N for N sites even in the limit of excluding D^{+2} and A^{-2} sites. When long-range Coulomb interactions are neglected, the generalization of the Mulliken dimer to the solid involves nearest-neighbor transfers of electrons, with spin conservation, thus producing D^+ holes and A^- electrons relative to the neutral, *DA* state. The self-consistent inclusion[5] of long-range, three-dimensional Coulomb interactions involves a renormalization of the energy -2δ. This does not alter the *VB* procedure of finding the proper linear combination of all possible *VB* structures.

The N sites in a cyclic stack are labeled consecutively, with *Ds* at odd n and *As* at even n. The electron-hole vacuum $|0\rangle = |\ldots DADA \ldots\rangle$ is a neutral, diamagnetic state with total spin $S = 0$. The site representation[13] for crystal-perturbed states is extended to hole operators $c_{n\sigma}^+$ creating $|D^+\bar{\sigma}\rangle$ sites at odd n and electron operators $c_{n\sigma}^+$ creating $|A^-\sigma\rangle$ sites at even n. Excluding D^{+2} and A^{-2} and measuring energy from $|0\rangle$ gives the basic *CT* hamiltonian

$$h_{\text{red}} = -\mathscr{H}_0/\sqrt{2}|t| = z \sum_{n\sigma} c_{n\sigma}^+ c_{n\sigma} + \sum_n [(n, n+1)^+ + (n+1, n)] \quad (4)$$

where $z = \delta/\sqrt{2}|t|$ and the operators $c_{n\sigma}^+$, $c_{n\sigma}$ are fermions. They measure the total number of ionic sites, whether D^+ or A^-, and lead to

$$\gamma(z) = N^{-1}\left\langle \sum_{n\sigma} c_{n\sigma}^+ c_{n\sigma} \right\rangle = N^{-1} \frac{\partial}{\partial z} \langle h_{\text{red}} \rangle \quad (5)$$

for *CT* in the ground state. Nearest-neighbor *CT* interactions between spin-paired electrons are described by the operator $(n, n+1)^+$

$$(n, n+1)^+ \equiv (c_{n\alpha}^+ c_{n+1\beta}^+ + c_{n\beta}^+ c_{n+1\alpha}^+)/\sqrt{2} \quad (6)$$

$(n, n+1)^+|0\rangle$ is a normalized singlet[1] $|D^+A^-\rangle$ electron-hole pair at n and $n + 1$. We assign a ket like $|0\rangle$ to every possible choice of A, $A^-\alpha$, $A^-\beta$ at even n and of D, $D^+\alpha$, $D^+\beta$ at odd n. For a ring of N sites, electroneutrality requires that the $\binom{N/2}{p}$ ways of producing p cations $D\,\sigma^+$, each with spin degeneracy 2, be matched by precisely $\binom{N/2}{p}$ anion radicals $A\,\sigma^-$. There are consequently almost 16,000 *VB* structures[5] participating in the configuration interaction for $N = 10$. Exact subspaces of S and k, with wavevector $k = 0$, $\pm 2\pi/N, \ldots, \pi$ for a ring of N sites, greatly reduce these dimensions. Thus h_{red} spans 73, 75, and 98 symmetry-adapted *VB* kets, respectively, in the $\{0, 0\}$, $\{0, \pi\}$ and $\{1, \pi\}$ subspaces for $N = 10$. The *VB* analysis of h_{red} in exact $\{S, k\}$ subspaces has been carried out[5] by generalizing the Rumer–Pauling[10] diagrammatic approach to conjugated molecules.

The main results[5] are (a) the $k = 0$ singlet derived from the neutral state is the absolute ground state for $z < z_c = 0.53 \pm 0.01$ where $\gamma(z_c) = 0.68 \pm 0.01$; the $k = \pi$ singlet associated with the ionic state is the absolute ground state for $z > z_c$; (b) the system is diamagnetic, with a finite ΔE_m, for $z < z_c$ and becomes paramagnetic, with $\Delta E_m = 0$, for $z > z_c$. Thus the diamagnetic-paramagnetic transition corresponding to the vanishing of ΔE_m is also signaled by a change of symmetry in the ground state. Any *CT* solid with a mixed regular stack and $\gamma < \gamma(z_c) = 0.68 \pm 0.01$ is rigorously predicted, at least for h_{red} given in Eq. 4, to have $\Delta E_m > 0$. The TMPD-TCNQ gap of 0.07 ev corresponds to $\gamma \sim 0.60$–0.65 when the typical value of $\sqrt{2}|t| \sim 0.3$ ev is assumed.[5] The larger $\Delta E_m \sim 0.13$ ev in TMPD-Chloranil or PD-Chloranil would imply slightly lower γ.

Collective effects due to long-range, three-dimensional Coulomb interactions are included self-consistently in the Hartree approximation and produce a first-order transition, with discontinuous $\gamma(z)$, when the critical value $m/\sqrt{2}|t| = 1.4 \pm 0.1$ of the Madelung stabilization per D^+A^- dimer is exceeded.[5] For $m/\sqrt{2}|t| < 1.4$, the variation of $\gamma(z)$ around z_c becomes more rapid, but the magnetic gap ΔE_m still opens up for $z < z_c = 0.53$. The self-consistent treatment of Coulomb interactions thus modifies the functional dependence of γ on $z = \delta/\sqrt{2}|t|$, but does not change the value of the diamagnetic-paramagnetic transition.

III TMPD-TCNQ

The crystal structure[14] and physical properties[1] of TMPD-TCNQ clearly point to a predominantly ionic solid. The exact degree of *CT* in mixed $\ldots D^{+\gamma}A^{-\gamma}D^{+\gamma}A^{-\gamma}\ldots$ stacks has nevertheless been difficult to measure accurately. For example, the structural differences[15] between neutral TCNQ or TMPD and ionic TCNQ$^-$ or TMPD$^+$ observed by X-rays gives a rough estimate for γ. But the small changes in bond lengths and the comparable changes due to the crystalline environment preclude accurate determinations. Direct optical and i.r. methods are even more approximate, as the spectra are merely compared to those of known neutral or ionic compounds.

Van Duyne and Suchanski[7] have recently domonstrated that resonance Raman (RR) is an accurate and versatile tool for determining γ in various TTF (tetrathiofulvalene) and TCNQ salts. RR probes specific intramolecular vibrations, some of which are sensitive to the molecular charge. Thus the exocyclic carbon stretch[7] of TCNQ°, which is around 1453 cm^{-1} for the quinoidal form in the neutral solid, shifts to 1389 cm^{-1} in the more benzenoid TCNQ$^-$ ion-radical generated electrolytically. A shift of over 60 cm^{-1}

TABLE I

Exocyclic carbon stretch in $TCNQ^{-\gamma}$ systems.

System	$h\nu(\text{obs})^a$	γ (Eq. 7)
$TCNQ^\circ$(solid)	1453	0.00^b
$TCNQ^-$(soln)	1389	1.00^b
$TEA(TCNQ)_2$	1421	0.50
$Q(TCNQ)_2$	1425	0.44
TMPD-TCNQ	1407	0.70

[a] *RR* data from Ref. 7, in cm^{-1}.

[b] Fit is automatic, defines Eq. (7).

and a resolution of 1 cm^{-1} clearly makes RR a promising tool for measuring γ in the solid state. The relatively high-energy intramolecular modes are apparently insensitive to the crystalline environment. Finally, shifts in several intramolecular vibrations can usually be followed although the exocyclic carbon stretch considered below provides the greatest variation between $TCNQ^\circ$ and $TCNQ^-$.

Table I shows observed[7] energies for the exocyclic stretch. Crystalline TCNQ, which necessarily corresponds to $TCNQ^\circ$, yields the value for $h\nu(0) = 1453$ cm^{-1}. The $TCNQ^-$ ion-radical in solution gives $h\nu(1) = 1389$ cm^{-1}. A linear interpolation of $h\nu(\gamma)$ gives

$$h\nu(\gamma) = h\nu(0) - 64\gamma \tag{7}$$

The triethylammonium (TEA) salt has the 1 : 2 stoichiometry $TEA(TCNQ)_2$ which for TEA^+ requires $\gamma = 1/2$ for the TCNQ stack. The observed and calculated vibration of 1421 cm^{-1} agree exactly. The 1 : 2 conductor based on quinolinium may have slightly less than $\gamma = 1/2$. When both TTF and TCNQ modes are probed,[7] the *RR* result for the important conductor TTF-TCNQ is $\gamma = 0.56 \pm 0.11$, which is good agreement with the $\gamma = 0.59$ value deduced from superlattice scattering.[16]

Although a definitive assessment of *RR* determinations of γ will probably involve further systematic studies and comparisons with other physical data, there can be little doubt that the TMPD-TCNQ vibration[7] at 1407 cm^{-1} in Table I demonstrates a less than completely ionic lattice, with $\gamma \sim 0.70$. Previous difficulties[17] in accounting for a finite magnetic gap in mixed regular stacks were based on $\gamma = 1$ and Heisenberg exchange in the resulting ion-radical stack. Such a model is now untenable. The *VB* analysis[5] of arbitrary $\gamma(z)$ for finite bandwidth $|t| = \delta/\sqrt{2}z$ demonstrates finite ΔE_m for $\gamma < \gamma_c = 0.68$. As discussed above, the $\Delta E_m \sim 0.07$ ev for TMPD-TCNQ leads to $\gamma \sim 0.60 - 0.65$, depending on various estimates for the Coulomb interactions in the parameter $m/\sqrt{2}|t|$. The agreement for γ is well within the experimental uncertainties and the theoretical approximations.

Since TMPD-TCNQ has the best donor and acceptor, as well as the smallest ΔE_m, of the few 1 : 1 complexes with mixed regular stacks,[1] it is likely that the "ionic" complexes TMPD-Chloranil or PD-Chloranil have $\gamma < 0.7$. This could be checked by resonance Raman spectroscopy, although the vibrations of Chloranil$^{-\gamma}$, TMPD$^{+\gamma}$, or PD$^{+\gamma}$ would have to be calibrated for the degree of *CT*. Furthermore, it would clearly be desirable to find a more ionic complex in order to verify the prediction of vanishing ΔE_m for $\gamma \sim 1$.

IV DISCUSSION

The *VB* approach to organic *CT* complexes with mixed *DA* stacks can readily be generalized to alternating transfer integral $\ldots t_1 t_2 t_1 t_2 \ldots$ along the chain, as occur[8] in various 1:1 complexes of substituted phenazines and TCNQ. The lowest *CT* excitation of the model and the rigid-lattice energy gap for semiconduction are also natural extensions. It is quite likely that various generalizations, such as including different types of phonons or additional electrostatic interactions, to h_{red} in Eq. (4) will be necessary. The fact that exact numerical solutions to h_{red} are now possible for finite rings permits the rigorous assessment of results even for infinite stacks. The exact *VB* treatment of correlations in mixed regular *DA* stacks clearly improves[5] on previous approximate many-body results.

It is consequently natural to consider *VB* methods in other narrow-band systems. Segregated stacks of the type $\ldots A^{-\gamma}A^{-\gamma}A^{-\gamma}A^{-\gamma}\ldots$ or $\ldots D^{+\gamma}D^{+\gamma}D^{+\gamma}D^{+\gamma}\ldots$ occur in ion-radical salts and organic conductors.[1,9] A large variety of structures and partial charges is realized for various TCNQ and TTF systems. Conductors typically have $\gamma < 1$, or fewer electrons N_e than sites N, and a single site per unit cell, leading to a single *CT* integral t. Various modifications of Hubbard models have been proposed,[1,9]

$$\mathscr{H} = t \sum_{n\sigma} (a_{n\sigma}^{+} a_{n+1\sigma} + a_{n+1\sigma}^{+} a_{n\sigma}) + U \sum_{n} a_{n\alpha}^{+} a_{n\beta}^{+} a_{n\beta} a_{n\alpha} \tag{8}$$

Here $a_{n\sigma}^{+}$, $a_{n\sigma}$ are fermion operators for electrons and $U > 0$ is a measure of *CT* excitations of the type $A^{-}A^{-} \rightarrow A^{-2}A$ or $D^{+}D^{+} \rightarrow D^{+2}D$ in which two spin-paired electrons at a site are created. The thermodynamics of Eq. (8) for $N_e < N$ have only been carried out[18] in the atomic limit $U \gg t$. Unfortunately, the atomic limit implies a Curie-law magnetic susceptibility $\chi(T)$, which is not even in qualitative agreement with experiment. Corrections[19] of order t^2/U lead to antiferromagnetic spin correlations, but the Heisenberg AF also does not fit the observed[20] $\chi(T)$ in conductors.

The CT excitation in mixed and segregated stacks is associated $|2\delta|$ and U, respectively, in the limit $t \rightarrow 0$. CT bands in both types of stacks occur[1] around 1 ev. Since finite t effects were shown to be important in mixed stacks, they should also be important in segregated stacks. The VB prescription is to assign a diagram with each possible distribution of N_e electrons on N sites arranged in a circle. There are again a large number of diagrams, especially if doubly occupied A^{-2} or D^{+2} sites are included. Since the failure of the atomic limit is associated with the exclusion of A^{-2} or D^{+2} sites, it is important to retain them for realistic $\chi(T)$ computations.

Doubly-occupied sites at energy U have paired spins. The transfer operators

$$\begin{aligned} (n, n+1)^{+} &\equiv (a^{+}_{n+1\alpha} a_{n\alpha} + a^{+}_{n+1\beta} a_{n\beta})/\sqrt{2} \\ (n+1, n) &= (a^{+}_{n\alpha} a_{n+1\alpha} + a^{+}_{n\beta} a_{n+1\beta})/\sqrt{2} \end{aligned} \tag{9}$$

move electrons to the right and left, respectively, while conserving spin. They create normalized singlet-correlated $A^{-}A^{-}$ sites when acting on $A^{-2}A$ or AA^{-2}, much the same way as the electron-hole operators defined in Eq. (6) for mixed stacks. Indeed, ion-radical stacks are self-complexes whose lowest electronic excitation is again a CT, rather than a localized, excitation.[1]

The enumeration of VB diagrams for finite chains of N sites with $N_e < N$ electrons is straightforward.[21] The resulting VB structures are spin and symmetry adapted to produce exact $\{S, k\}$ subspaces for Hamiltonians like $\mathscr{H}/\sqrt{2}|t|$. The parameter $U/\sqrt{2}|t|$ now controls the interplay between band ($U = 0$) and localized ($t = 0$) effects.

The neglect of all intersite Coulomb interaction in Eq. (8) can only be justified for strongly-screened electrons. This probably is not the case for narrow-band one-dimensional organic conductors. The VB procedure potentially includes intersite effects, which are diagonal and can be obtained by inspection of the VB structures. However, the current limitation of numerical work on finite ($N \leq 10$) chains and extrapolations to large N are not well suited for more than interactions between a few neighbors. We have sought to model intersite interactions by excluding all VB diagrams with any $A^{-2}A^{-2}$ or $A^{-2}A^{-}$ neighbors. Their energies of $4M_1$ and $2M_1$, respectively, clearly exceed the on-site repulsion U when, as for π-radicals, the nearest-neighbor interaction M_1 is only slightly smaller than unrenormalized U_0. Then U in Eq. (8) is essentially $U_0 - M_1 > 0$. The exclusion of such VB diagrams also has the practical advantage of significantly reducing the size of the VB basis. Thus thermodynamic quantities like $\chi(T)$ or the magnetic heat capacity can be computed[21] rigorously for small segregated rings. It remains to be seen whether rings of $N \leq 12$ suffice, as in the Heisenberg AF[4], for the thermodynamics of the infinite chain.

In summary, we emphasize that *VB* methods are exact in the non-overlapping $t \rightarrow 0$ of isolated molecular sites. Since Eq. (4) is solved exactly, they provide a complete description of electron correlations for small *t*, where comparable band (*MO*) computations would involve prohibitively large amounts of configuration interactions. In the present context of model Hamiltonians with fixed parameters (t, δ, or U) and a few states per site, the *VB* basis is complete and potentially exact. The possibility of subspaces with fixed total spin and the high symmetry of partly-filled organic conductors, usually with a single site per unit cell along the stack, and of 1 : 1 *CT* salts greatly simplifies the diagrammatic *VB* analysis which otherwise would involve enormous basis sets of over 10^4 for $N \sim 10$–12 sites. For the narrow bands appropriate to π-molecular organic solids, *VB* results offer consistent improvements over such standard solid-state methods as the random phase approximation. The demonstration of incomplete *CT*, with $\gamma \sim 0.6$–0.7, in $\mathrm{TMPD}^{+\gamma}\mathrm{TCNQ}^{-\gamma}$ resolves a difficult old problem and illustrates the power of solid-state *VB* methods.

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