Effective π-electron Hamiltonian for small-radii nanotubes: novel interpretation of curvature-induced conductivity of the (5,0) carbon nanotube

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Abstract

A subsystem, even if strongly interacts with its environment, can be described by an effecive Hamiltonian whose eigenvalues are precisely the same as the selected eigenvalues of the total system. We apply this principle to develop an energy-independent partitioning scheme extracting an effective π-electron model from valence Hamiltonians. The technique is used to explain the metallic band structure of nanotubes with small diameter, e.g., the (5,0) tube, showing that the increased curvature enhances second and third neighbor hopping interactions which are directly responsible for the metallic features in these systems.

Large quantum systems with many degrees of freedom are usually impossible to treat exactly. One may consider a smaller part of the system, to be henceforth called a subsystem, for which the Schrödinger equation is easier to solve, and which serves as a model of the full system. If the subsystem and its complement system (environment) interact with each other, the treatment of the isolated sub-part will only be approximate.

Using the theory of effective Hamiltonians and the Bloch equation, it is, however, possible to construct a much more realistic model for the subsystem, which possesses energy levels that match exactly some selected levels of the total system. In this Letter we apply this philosophy to the example of small-radii carbon nanotubes, where the σ and π subsystems are interacting, thus a naive treatment of an isolated π sub-part is known to produce unrealistic results. However, we construct an effective π-electron Hamiltonian which has exact energy levels, with full account of the σ-π mixing. The approach used by us allows reasonably strong σ-π mixing, while retaining the conceptual simplicity of a simple π-electron description.

Electronic structure of a carbon nanotube with large diameter can be qualitatively described by deriving it from graphene bands using simple zone-folding arguments[1]. For example, among $(n,0)$ tubes those for which n is divisible by 3 are expected to be metallic, while others have a gap at the Fermi level. It is well known, however, that these simple arguments break down completely for highly curved tubes, and are violated even for moderate curvature. The (5,0) tube, for example, is, in fact, metallic with a high density of states at the Fermi level[2, 3]. The reason of this anomalous behavior is clearly in the high curvature of small-radii tubes, which prevents one to apply, not only simple zone-folding arguments, but also $\sigma - \pi$ separation. One of the first studies which called attention to the extreme importance of $\sigma - \pi$ hybridization effects in small tubes was published by Blase et al. [4].

In this Letter, we derive an effective π-electron Hamiltonian for the (5,0) tube which exactly accounts for the $\sigma - \pi$ mixing, and use it to reinterpret the band structure. In particular, we show that the enhanced second neighbor matrix elements are responsible for the the metallic band structure.

The mathematical tool we use to get the effective Hamiltonian in the π-electron subspace is based on the Bloch equation[5–10] or the equivalent energy-independent partitioning technique[11]. The essence of the theory, as applied to the present problem of defining an effective π Hamiltonian, can be formulated as follows. Let $\{\varphi_i\}_{i=1}^n$ be n π orbitals on a curved system, oriented into a direction locally perpendicular to the surface. Let $\{\psi_i\}_{i=1}^n$

be n exact orbitals in the sense that $\varepsilon_i = \langle \psi_i | H | \psi_i \rangle$ are exact eigenvalues of the full $(\sigma + \pi)$ Hamiltonian H. The interrelation matrix between these orbital sets is

$$T_{ik} = \langle \varphi_i | \psi_k \rangle.$$

If both sets are orthonormalized, the Bloch wave operator which transforms the pure π functions φ_i to the exact ones is given by[10]

$$\Omega = \sum_{ik=1}^{n} | \psi_i \rangle \, (T^{-1})_{ik} \, \langle \varphi_k |$$

which gives rise to the effective Hamiltonian

$$H_{\mu\nu}^{\text{eff}} = \langle \varphi_\mu | H \Omega | \varphi_\nu \rangle. \tag{1}$$

It is easy to see that the eigenvalues of this effective Hamiltonian, whose dimension is reduced to the number of π sites, coincide with n exact levels of the full Hamiltonian. This follows from expanding the above formula to yield

$$H_{\mu\nu}^{\text{eff}} = \sum_{i=1}^{n} \varepsilon_i \, T_{\mu i} (T^{-1})_{i\nu} \tag{2}$$

which is the projected spectral decomposition of the exact Hamiltonian. The same formula was derived by matrix partitioning technique in Ref.[11]. Note that H^{eff} is not Hermitian, but its eigenvalues are still real numbers.

Based on the above equations, we devised the following procedure:

- We set up a valence-electron one-particle Hamiltonian

$$H = \sum_{\mu\nu}^{(\sigma+\pi)} V_{\mu\nu} \left(a_{\mu\uparrow}^\dagger a_{\nu\uparrow} + a_{\mu\downarrow}^\dagger a_{\nu\downarrow} \right) \tag{3}$$

for the unit cell of an (5,0) tube. Labels μ, ν run over all valence orbitals of the tube, thus H contains all $\sigma - \pi$ effects and predicts the correct (metallic) band structure (Fig. 1). Parameters for $V_{\mu\nu}$ were taken from Pople[12]. (In course of the band structure calculations, interactions between neighboring unit cells were only taken into account. This approximation is justified by the near-sightedness of $V_{\mu\nu}$.) This band structure agrees well with the prediction in Ref.[3], and less well with the DFT calculation by Kürti et al.[13], where the bands are split due to electron interaction neglected by (3).

- We apply a hybridization transformation mixing the $2s$ and $2p$ orbitals on each carbon, pointing three σ hybrids to their neighbors and forming the fourth quasi π orbital in the direction locally perpendicular to the σ ones. The resulting quasi π hybrids were found to have nonzero s-characters due to curvature effects: they can be described as sp^{15} orbitals (instead of sp^{∞}). The bare integrals $V_{\mu\nu}$ are transformed to the integrals over hybrids, $U_{\mu\nu}$.

- We pick up the above quasi-π hybrids and define a quasi-π Hamiltonian as the corresponding block of H:

$$H^{\text{quasi-}\pi} = \sum_{\mu\nu}^{(\pi)} U_{\mu\nu} \left(a_{\mu\uparrow}^{\dagger} a_{\nu\uparrow} + a_{\mu\downarrow}^{\dagger} a_{\nu\downarrow} \right)$$

  The band structure of an (5.0) tube as obtained by this quasi-π Hamiltonian is shown in Fig.2. Interestingly, although the Hamiltonian expressed in terms of integrals $U_{\mu\nu}$ is defined over the π-block and has nonzero interaction with the hybridized σ block, the resulting quasi-π band structure is still physically correct, i.e., it describes a metal. Differences between the band structures shown in Figs. 1 and 2 are due to the effective $\sigma - \pi$ interaction. The similarity of the two figures shows that it is not too large even for an (5,0) nanotube.

- Substituting integrals $U_{\mu\nu}$ over hybrids with the matrix elements of the effective Hamiltonian of Eq. (1) or (2), we get again the "exact" band structure shown in Fig.1. In applying Eq.(2), we selected those levels i $(i = 1, 2, \ldots n)$ whose wave functions have maximum projections to the quasi-π hybrids pointing to normal directions to the tube surface. The obtained band structure is *exact* at the Fermi level, though it is obtained from a calculation where the order of the final matrix diagonalized is determined only by the size of the π-space.

- Finally, the standard Hückel-type Hamiltonian using merely on-site and first-neighbor matrix elements is known to produce an incorrect band structure with a significant gap at the Fermi level, see Fig. 3.

The above consideration suggest that if the π orbitals are oriented to locally normal directions, a simple π-electron Hamiltonian is capable of describing the anomalous metallicity of small-radii tubes. The essential difference between the Hamiltonians used to produce Figs.

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2 and 3 is that in the latter case only first-neighbor interactions were taken into account. We can thus formulate the conjecture that the anomaly takes place due to *enhanced second-, third-, etc. neighbor interactions.* To cross-check this, we computed the band structure in the full valence space, i.e., taking into account all $\sigma - \pi$ interactions exactly, but neglected all but first-neighbor matrix elements in the valence Hamiltonian (3). The result is presented in Fig 4, showing a completely improper band structure, more similar to the simple Hückel result of Fig. 3. (A similarly wrong band structure is obtained if deleting second neighbor interactions form the effective π-electron Hamiltonian.) We can consider this as a proof of the conjecture.

The above analysis can be used to extract parameters for an effective π-electron Hamiltonian. In other words, the exact, system-dependent matrix elements $H_{\mu\nu}^{\text{eff}}$ can be substituted by standardized integrals $W_{\mu\nu}$ while preserving the most important features of the band structure. For (n,0) tubes such a parametrization is shown in the third line of Table 1, in comparison to the corresponding matrix elements in planar graphene and the undressed, bare matrix elements of the (5,0) tube. The enhancement of second neighbor interactions due to dressing, roughly by a factor of two, is well shown by the difference between the second and third lines. A significant (10–20%) enhancement of third-neighbor effects can also be observed. Importance of second and third neighbor effects in nanotubes was also pointed out in [15], here we emphasize their increase due to curvature. Performing the energy-independent partitioning technique and dressing the π-electron Hamiltonian by the parameters obtained, one not only gets a π-electron method with a predictive power for small-radii tubes or other highly curved systems, but one can also understand the basic features of the resulting integrals $W_{\mu\nu}$, pointing out the most important effects of the curvature. We performed the calculation for the (5,0) tube with the effective parameters shown in the third row of Table 1. The resulting Hückel band structure is depicted in Fig.5 which shows an acceptable agreement with the exact result presented in Fig.1.

To summarize,

1. it is possible to set up, even for highly curved conjugated systems, a one-electron-per site (quasi π) model Hamiltonian which accounts for $\sigma - \pi$ interactions implicitly, while still predicts proper electronic structure

2. curvature effects in such a quasi π Hamiltonian will be manifested in enhanced second-

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and higher-neighbor interactions

3. The philosophy we applied here is quite general: treating a subsystem which interacts with its environment, the unperturbed form of the Bloch equation defines an effective Hamiltonian for the subsystem possessing energy levels that match exactly those of the full system. The analysis of the structure of this effective Hamiltonian reveals the nature of the interaction in detail, and permits one to formulate simple models of practical significance.

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TABLE I: Representative Hamiltonian matrix elements. The term "vertical" refers to bonds parallel to the tube axis z. For 2nd and 3rd neighbors, it indicates large differences between the z coordinates of the involved atoms

System	diagonal	1st neighbor		2nd neighbor		3rd neighbor	
		vertical	non-vertical	vertical	non-vertical	vertical	non-vertical
graphene	-5.1856	-2.4594	-2.4594	-0.3349	-0.3349	-0.1473	-0.1473
(5,0) tube, bare π block	-6.3528	-1.9958	-1.7664	-0.6201	-0.1510	-0.2908	-0.3383
(5,0) tube, dressed π block	-5.5274	-1.8055	-1.9731	-1.0362	-0.3330	-0.3611	-0.3721

Figure Legends

Figure 1.

The band structure of the (5,0) tube at the Fermi level with either (i) the valence-electron Hamiltonian or (ii) the effective π-electron Hamiltonian. The energies are shifted to set the Fermi energy zero.

Figure 2.

The band structure of the (5,0) tube at the Fermi level with the hybridized bare (undressed) quasi-π block of the valence-electron Hamiltonian. The energies are shifted to set the Fermi energy zero.

Figure 3.

The Hückel band structure of the (5,0) tube at the Fermi level The energies are shifted to set the Fermi energy zero. First-neighbor matrix elements were bond-length dependent (see Ref.[14]).

Figure 4.

All-valence electron band structure of the (5,0) tube at the Fermi level neglecting all but first-neighbor hopping integrals. The energies are shifted to set the Fermi energy zero.

Figure 5.

Hückel band structure of the (5,0) tube at the Fermi level obtained by the effective parameters of the energy-independent partitioning technique. The energies are shifted to set the Fermi energy zero.