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Probing electronic excitations in molecular conduction

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We identify experimental signatures in the current-voltage (I-V) characteristics of weakly contacted molecules directly arising from excitations in their many electron spectrum. The current is calculated using a multielectron master equation in the Fock space of an exact diagonalized model many-body Hamiltonian for a prototypical molecule. Using this approach, we explain several nontrivial features in frequently observed I-Vs in terms of a rich spectrum of excitations that may be hard to describe adequately with standard one-electron self-consistent field theories.

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Theoretical efforts to model molecular conduction have largely been based on self-consistent field (SCF) models for electron-electron interactions.[1–4] While they have been fairly successful in describing both shapes and magnitudes of various I-V characteristics,[5,6] notable exceptions include low-temperature measurements on unconjugated and weakly coupled molecules,[7–10] as well as short conjugated molecules,[11] where there are clear disagreements between theory and experiment. Some disagreements could be attributed to uncertainties in geometry or parasitic resistances; nevertheless the applicability of SCF approaches needs to be scrutinized, especially in the weak coupling regime. Charging energies of short molecules ($\sim$3 eV for benzene) are often larger than their contact induced broadenings ($\leqslant$0.2 eV for benzene dithiol on gold), while couplings between various molecular units ($\sim$2 eV for conjugated molecules, much less for nonconjugated species) can be tuned widely using synthetic chemistry. A molecule could lie in a unique transport regime where its single-electron charging energy exceeds all other energy scales, even at room temperature, making it debatable whether it is better described as a *quantum wire* in the SCF regime, or as a *quantum dot* in the Coulomb blockade (CB) regime.

In this paper, we employ a multielectron master equation[12–14] in the Fock space of a prototypical molecular Hamiltonian to describe conduction through molecules with weak contact couplings or poor conjugation. A full many-body treatment of transport even with a small molecule, modeled simply as an array of quantum dots, yields many features with compelling similarities (Fig. 1) to relevant experiments.[7–9] These features, however, are quite difficult to obtain using a traditional nonequilibrium Green's function (NEGF) treatment of transport, being only *perturbative* in the interaction parameter.[15] A spin restricted (RSCF) calculation [inset in Fig. 1(c)] typically creates slow current onsets spread over several volts by Coulomb costs for adiabatic charging. The high zero-bias conductances, in clear variance with experiments, could be removed by incorporating self-interaction correction for integer charge addition in the CB regime. However, crucial to experiments in this regime is the fact that the molecule can also execute transitions between various *excited states* of the neutral and singly charged species *at no additional Coulomb cost*, making it possible to directly probe a rich spectrum of such transition levels within a small bias window.

It seems difficult to capture this rich spectrum adequately within any SCF theory even with self-interaction correction[17,18,20] or effective one electron potentials,[18,21] especially under nonequilibrium conditions. A single spin-degenerate level (Fig. 2) illustrates the problem. We start with a many-body Hamiltonian in a localized, orthogonal atomic basis set

$$\hat{H}=\sum_{\alpha}\epsilon_{\alpha}n_{\alpha}+\sum_{\alpha\neq\beta}t_{\alpha\beta}c_{\alpha}^{\dagger}c_{\beta}+\sum_{\alpha}U_{\alpha\alpha}n_{\alpha\uparrow}n_{\alpha\downarrow}+\frac{1}{2}\sum_{\alpha\neq\beta}U_{\alpha\beta}n_{\alpha}n_{\beta}, \tag{1}$$

where α,β denote the basis functions within a tight binding formulation, with ϵ, t, and U denoting onsite, hopping, and charging terms. The deficiencies of SCF (e.g., adiabatically smeared steps) can be rectified with self-interaction corrections using a spin unrestricted calculation (USCF)

$$\tilde{\epsilon}_{\alpha\sigma}=\langle\partial\hat{H}/\partial n_{\sigma}\rangle=\epsilon_{\alpha}+U_{\alpha\alpha}\langle n_{\alpha\bar{\sigma}}\rangle+\sum_{\beta}U_{\alpha\beta}\langle n_{\beta}\rangle, \tag{2}$$

where σ denotes the spin and $\tilde{\epsilon}_{\alpha}$s denote the mean-field onsite energies. For a single spin degenerate level, equilibrium properties and currents are calculated using the NEGF formalism[19,20] with a modified Green's function to account for self-interaction correction:

$$G_{\sigma}=(E-\epsilon-U\langle n_{\bar{\sigma}}\rangle-\Sigma)^{-1}, \tag{3}$$

where Σ is the contact self-energy. While, this calculation yields the right *equilibrium* properties such as $N-\mu$ [Fig. 2(b)], the same approach gives the wrong *nonequilibrium* properties such as current step heights. A simple unrestricted calculation yields equal step heights for each spin removal, while the exact result using rate equations predicts that the first step is two-thirds of the second [Fig. 2(c)], because there are two ways of removing (adding) the first spin for a filled (empty) level, but only one way to remove (add) the second one [Fig. 2(a)]. The SCF approach misses the fact that subsequent spin addition/removal processes need not contribute

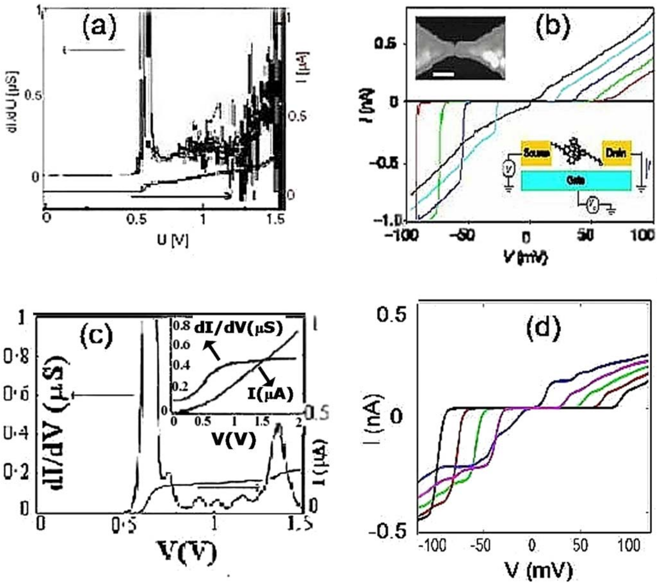

FIG. 1. (Color online) [(a) Reprinted with permission from J. Reichert, H. B. Weber, M. Mayor, and H. v. Lohneysen. Appl. Phys. Lett. 82, **4137**, copyright 2003, American Institute of Physics; (b) Reprinted by permission form Macmillan Publishers Ltd: J. Park, A. N. Pasupathy, J. I. Goldsmith, C. Chang, Y. Yaish, J. R. Petta, M. Rinkoski, J. P. Sethna, H. D. Abruna, P. L. McEuen, and D. C. Ralph, Nature 417, **722**, copyright (2002)]" (a), (b) Experimental and (c), (d) theoretical I-Vs for a molecular ring weakly coupled with a backbone or with conducting electrodes. Many nontrivial features such as low zero-bias conductance, sharp current onset, and a subsequent quasilinear region spanning several volts with multiple closely spaced features (a)–(d) arise from excitations in our treatment of CB. Such features, however, do not arise even qualitatively in a spin-restricted SCF (RSCF) treatment for the same parameter set[30] [inset in (c)], or from an orthodox Coulomb Blockade theory that does not capture size quantization and the physics of excitations. For asymmetric contacts, there are additional features (b), (d) including current step heights (as opposed to widths) that are asymmetric in bias, are modulated with a gate voltage,[7] and reverse polarity for gate voltages on either side of the charge degeneracy point.[16] Electron-phonon interactions smoothen out the first few low-energy plateaus, but are typically inadequate for generating the unique higher energy features.

equally to the overall current. The situation is exacerbated for strongly asymmetric contacts ($\gamma_L \gg \gamma_R$), where the difference in addition and removal pathways (two removal channels for positive bias on the left contact, vs one addition channel for negative bias) leads to a strongly asymmetric I-V with the first positive step being twice its negative counterpart (Fig. 3), as seen experimentally.[22]

It is worth noting that adding correlations within the SCF approach[20] (by replacing $\langle n_i n_j \rangle \approx \langle n_i \rangle \langle n_j \rangle [1-g_{ij}]$) merely alters the conductance plateau widths associated with the many-electron energies through the poles of the Green's function,[17,18] but it does not modulate the plateau heights associated with the rate constants between these levels driven by injection and removal by the contacts under bias (Fig. 3). In the weak coupling limit, the master equation in the Fock space of our exact diagonalized Hamiltonian naturally includes these higher order correlations. A hierarchical treatment of correlation effects within a one electron subspace may be possible, but it would necessarily require the evaluation of higher order Green's functions[23,24] extended to the nonequilibrium Keldysh contour, which effectively renormalizes the self-energies making them energy-dependent.

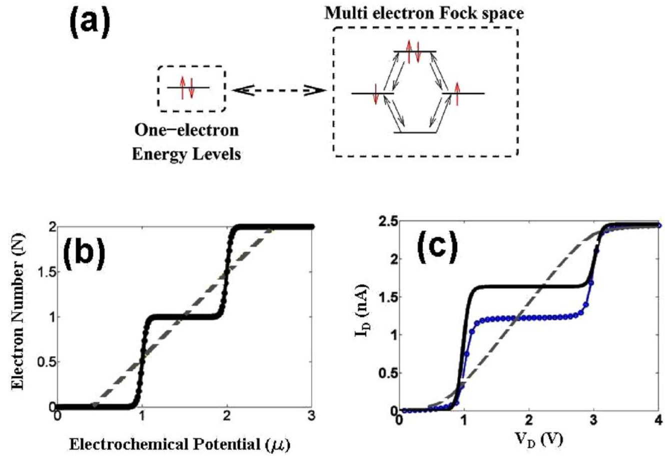

FIG. 2. (Color online) (a) Fock space, (b) equilibrium occupancy $N-\mu$ and (c) nonequilibrium I-V (assuming equal voltage division between contacts) of a spin degenerate level $\epsilon=1$ eV with a single electron charging energy $U=1$ eV. A spin restricted SCF calculation (gray dashed line) shows fractional charge occupation and is inappropriate in the weak coupling limit. An unrestricted SCF (blue line with circles) describes integer charge transfer and matches the many-body $N-\mu$ (black solid line) plot in (b); however, it yields *equal current steps* in (c) corresponding to sequential removal/addition of two electrons, as opposed to a many-body calculation in which step heights are in the ratio of 2:1. Including correlations in SCF alters the current onsets and the plateau widths, but misses the essential point that *consecutive removal/addition of spins need not carry equal current*.[12,22]

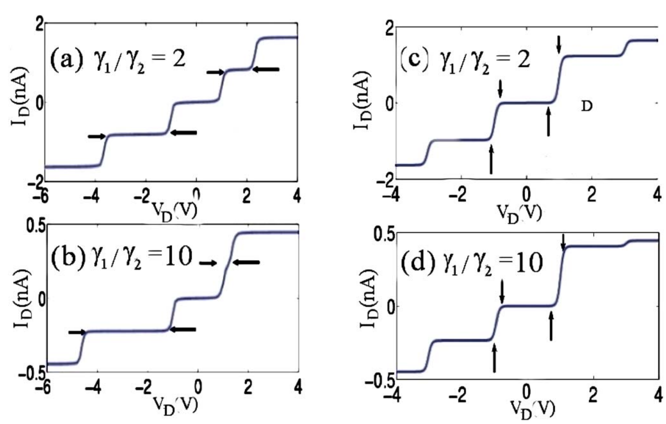

FIG. 3. (Color online) Comparison between SCF and Coulomb blockade type calculations. A spin unrestricted calculation (USCF) for γ_1/γ_2 equal to (a) 2 and (b) 10 yields varying plateau widths along the two bias directions consistent with RSCF calculations discussed in;[6] while maintaining the original ($\gamma_L=\gamma_R$) plateau heights. Contact asymmetry yields varying plateau heights as opposed to widths in a typical CB type calculation for the same parameter ratios (c) and (d).

The important point is that the inclusion of nonequilibrium correlation effects demands revisiting transport formalisms[25–28] rather than simply focusing on improvements in quantum-chemical methods.

The discrepancy with SCF becomes more pronounced with multiple orbitals, where a spin can be removed by one contact from the ground state and reinjected by the other into feasible excitations of the neutral and singly charged systems, causing additional features within the Coulomb blockade plateaus. Such excitations, crucial to the experiments addressed here, arise *nonperturbatively* from our rate equations through exact diagonalization of the many-body Hamiltonian, going beyond orthodox Coulomb blockade theory[29] due to size quantization and transitions among discrete many-body states. Since the size of multi-particle Fock space increases exponentially with the number of basis functions, we employ a minimal basis set in a reduced single-particle Hilbert space that captures the conjugation chemistry and yet allows exact diagonalization.[30] Quantitative justice to chemistry would require looking at a reduced subset of excitations (partial configuration interaction[25]) within a multiorbital description. Our aim is to solve the transport problem exactly for a simple system, rather than do an approximate SCF calculation of a more elaborate quantum chemical system.[31]

Approach. We start with a tight-binding model with one orbital per atom of benzene with parameters in Eq. (1) parameters that can be benchmarked with separate local-density approximation (LDA) calculations.[32] In contrast with single dot studies, long-ranged Coulomb terms (modeled with the Mataga-Nishimoto approximation[33]) and hopping are responsible for off-diagonal correlations in the charging term of the molecular eigenspace. Exact diagonalizing this Hamiltonian yields a large spectrum of closely spaced excitations in every charged molecular configuration. Using the equation of motion of the density matrix of the composite molecule and leads and assuming no molecule-lead correlations, one can derive[34,35] a simple master equation for the density matrix of the system. Ignoring off-diagonal coherences, we are left with a master equation[35] in terms of the occupation probabilities P_i^N of each N electron many-body state $|N,i\rangle$ with total energy E_i^N. The master equation then involves transition rates $R_{(N,i)\to(N\pm1,j)}$ between states differing by a single electron, leading to a set of independent equations defined by the size of the Fock space[12]

$$\frac{dP_i^N}{dt} = -\sum_j \left[R_{(N,i)\to(N\pm1,j)}P_i^N - R_{(N\pm1,j)\to(N,i)}P_j^{N\pm1}\right] \quad (4)$$

along with the normalization equation $\Sigma_{i,N}P_i^N=1$. For weakly coupled dispersionless contacts, parametrized using bare-electron tunneling rates γ_α, (α: left/right contact), we define the rate constants

$$\Gamma_{ij\alpha}^{Nr} = \gamma_\alpha |\langle N,i|c_\alpha^\dagger|N-1,j\rangle|^2,$$

$$\Gamma_{ij\alpha}^{Na} = \gamma_\alpha |\langle N,i|c_\alpha|N+1,j\rangle|^2, \quad (5)$$

$c_\alpha^\dagger, c_\alpha$ are the creation/annihilation operators for an electron on the molecular end atom coupled with the corresponding electrode. The transition rates are given by

$$R_{(N,i)\to(N-1,j)} = \sum_{\alpha=L,R} \Gamma_{ij\alpha}^{Nr}[1-f(\epsilon_{ij}^{Nr}-\mu_\alpha)],$$

$$R_{(N-1,j)\to(N,i)} = \sum_{\alpha=L,R} \Gamma_{ij\alpha}^{Nr} f(\epsilon_{ij}^{Nr}-\mu_\alpha) \quad (6)$$

for the removal levels $(N,i\to N-1,j)$, and replacing $(r\to a, f\to 1-f)$ for the addition levels $(N,i\to N+1,j)$. μ_α are the contact electrochemical potentials, f is the corresponding Fermi function, with single particle removal and addition transport channels $\epsilon_{ij}^{Nr}=E_i^N-E_j^{N-1}$, and $\epsilon_{ij}^{Na}=E_j^{N+1}-E_i^N$. Finally, the steady-state solution to Eq. (4) is used to get the left terminal current

$$I = \pm\frac{e}{\hbar}\sum_{ij}\left[R_{(N,i)\to(N\pm1,j)}^L P_i^N - R_{(N\pm1,j)\to(N,i)}^L P_j^{N\pm1}\right], \quad (7)$$

where states corresponding to a removal of electrons by the left electrode involve a negative sign.

Results. We calculate the current in a break-junction configuration with equal electrostatic coupling with the leads, $\mu_{L,R}=E_F\mp eV_d/2$, and equal resistive couplings set by fixing the voltage division ratio $\gamma=\gamma_L/\gamma_R=1$, $\gamma_L=0.6$ meV. The coulomb blockade with integer charge transfer manifests itself as a vanishing prethreshold current followed by a stepwise increase in current.[7–9,16] The onset of conduction is established by the offset between the equilibrium Fermi energy E_F and the first accessible transition energy [focusing on removal levels for concreteness, this corresponds to the transport channel marked ϵ_{00}^{Nr} in Figs. 4(a) and 4(b)]. The onset can be varied by varying the gate voltage, thereby accounting for the variation in the conductance gap[22] with a gate bias.

The simplest impact of the coulomb blockade on the I-Vs of short molecular wires is a clear suppression of zero-bias conductance, often seen experimentally.[11,36] Indeed, a spin unrestricted SCF with self-interaction corrections[17,18] can yield a Coulomb staircase with intervening plateaus through the Coulomb cost of adding or removing an electron to the molecular ground state. However, integer charge transfer can also occur between various electronic *excitations* of the neutral and singly charged species at marginal correlation costs.[37,38] The above fact leads to fine structure in the plateau regions,[7–10] specifically, a quasilinear regime resulting from very closely spaced transport channels (ϵ_{ij}^N) via excitations. The crucial step is the access of the first excited state via channel ϵ_{10}^{Nr}, following which transport channels involving higher excitations are accessible in a very small bias window. The sequence of access of transport channels upon bias, enumerated in the state transition diagrams shown in Figs. 4(a) and 4(b), determines the shape of the I-V. When the Fermi energy E_F lies closer to the threshold transport channel ϵ_{00}^{Nr} [Fig. 4(a)], it takes an additional positive drain bias for the source to access the first excited state of the neutral system via the transition ϵ_{10}^{Nr}, as shown in the state transition diagram in Fig. 4(a). The I-V shows a sharp rise followed by a plateau [Fig. 4(c), dotted line], as seen in various experiments.[39] However, when transport channels that involve low lying excitations such as ϵ_{10}^{Nr} are closer to the Fermi energy E_F than

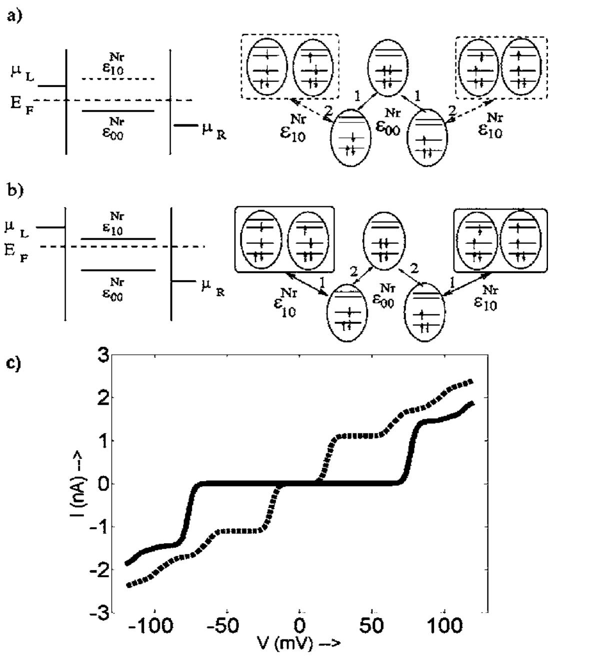

FIG. 4. Coulomb blockade I-V features for a general molecular system, showing transitions at threshold involving (1) only ground states. Here $|E_F-\epsilon_{00}^{Nr}|=10$ meV. ϵ_{00}^{Nr} is accessed before ϵ_{10}^{Nr} (shown in the adjacent state transition diagram). I-V characteristics [black dotted line in (c)] then has a brief intervening plateau until an excitation is accessed. (2) Threshold transition involving excited states. Current at threshold ($|E_F-\epsilon_{00}^{Nr}|=30$ meV) involves a transport channel involving excited states also (say ϵ_{10}^{Nr}) i.e., ϵ_{10}^{Nr} is accessed before ϵ_{00}^{Nr}. In this case (see text) current rise [black solid line in (c)] due to closely spaced excitations follows upon threshold.

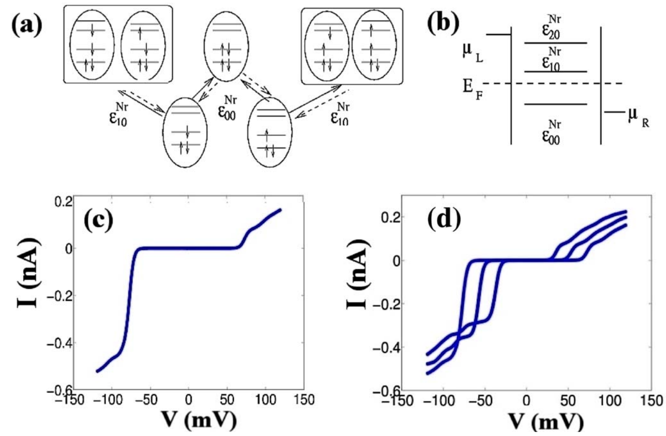

FIG. 5. (Color online) (a) State transition diagram showing various addition and removal pathways for asymmetric contacts ($\gamma_L \gg \gamma_R$), including the possibility of populating higher excitations (b), say, via transport channel ϵ_{20}^{Nr} at threshold. For positive bias charge removal is the rate limiting process, while for negative bias addition dominates, accounting thus for the corresponding I-V asymmetry in (c). Progressive access of higher excitations also accounts for the observed gate modulation of the current steps, as shown in (d).

ϵ_{00}^{Nr} [Fig. 4(b)], the excitations get populated by the left contact immediately when the right contact intersects the threshold channel ϵ_{00}^{Nr}, allowing for a *simultaneous* population of both the ground and first excited states via ϵ_{00}^{Nr} and ϵ_{10}^{Nr} at threshold. Under these conditions the I–V shows a sharp onset followed immediately by a quasilinear regime [Fig. 4(c) solid line] with no intervening plateaus, as observed frequently in I–Vs of molecules weakly coupled with a backbone.[7–9]

The direct role of excitations in conduction becomes particularly striking under asymmetric coupling ($\gamma=100, \gamma_L=0.6$ meV) with contacts.[7,16] In contrast to the SCF regime where unequal charging drags out the same level of current over different voltage widths,[6] in the CB regime the current step heights themselves are asymmetric at threshold [Fig. 5(c)]. This asymmetry arises due to the difference in the number of pathways for removing or adding a spin, also taking into account the possible excitation channels between the neutral and singly charged species [Fig. 5(a) and 5(b)]. The number of such accessible excitations at threshold can be altered with an external gate bias, leading to a prominent gate modulation of the threshold current heights, over and above the modulation of the onset voltages and the conductance gap[7] [Fig. 5(d)]. Furthermore, it is easy to show that the asymmetry will flip between gate voltages on either side of the charge degeneracy point, as is also observed experimentally.[16] While the qualitative features of our I-Vs are robust with respect to variation of our model parameters, details specific to experiments (e.g., onset voltages, polarization asymmetries,[8] and temperature dependences[9]) can vary and will be discussed in detail elsewhere.[32] For instance, correlation alone cannot explain ultralow peak currents through a level since those depend only on contact couplings through the ratio $\gamma_L\gamma_R/(\gamma_L+\gamma_R)$. This predicts a peak current ~ 3 μA for a 0.1 eV broadening as in chemisorbed benzene dithiol,[25] still much larger than some experiments,[11] indicating that one needs to further postulate weak couplings due to nonideal bondings at contacts or perhaps parasitic resistances due to multiple molecules.[40] Further complications could arise from strong electron-phonon interactions[7] that smoothen out the first few conduction plateaus in Fig. 1(d) due to low lying phonon excitations at tens of meV of energy, significantly smaller than their Coulomb counterparts.

In summary, we have used a rate equation in the Fock space of a molecular Hamiltonian to address significant experimental features like suppressed zero-bias conductances, sharp steps that are often asymmetric, gate modulated and interchangeable, and followed occasionally by extended quasiohmic regimes. While our method is particularly suited to systems with large charging and small coupling, the opposite regime is usually handled perturbatively by SCF-NEGF. Developing the transport formalism for the intermediate coupling regime could be nontrivial,[26,27] involving noval physics due to the interplay between charging (localization) and hybridization (delocalization), and may be crucial to understanding a variety of other molecular switching and sensing-based phenomena already being explored experimentally.

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[30] The features explained in the experiments are qualitatively independent of the quantum chemical model. For Fig. 1(c) we have used in our prototype molecular Hamiltonian, a single electron charging $U=2$ eV and a level separation $\Delta\epsilon=0.9$ eV, while for calculations on porphyrin based molecule [Fig. 1(d)] a charging energy of $U=100$ meV and $\Delta\epsilon=50$ meV were used.
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