Berry-phase effects in transport through single Jahn-Teller molecules

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The vibrational modes of Jahn-Teller molecules are affected by a Berry phase that is associated with a conical intersection of the adiabatic potentials. We investigate theoretically how this Berry phase affects transport through a single $E\otimes e$ Jahn-Teller molecule when the tunneling electrons continually switch the molecule between a symmetric and a Jahn-Teller distorted charge state. We find that the Berry phase in conjunction with a spectral trapping mechanism leads to a current blockade even in regions outside the Coulomb blockade. The blockade is strongly asymmetric in the gate voltage and induces pronounced negative differential conductance.

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The vision of molecular electronics has stimulated great interest in understanding transport through single molecule devices both experimentally [1, 2, 3, 4, 5, 6] and theoretically [7, 8, 9, 10, 11, 12, 13, 14]. The coupling of electronic degrees of freedom to few well-defined molecular vibrations, a property that discriminates transport through single molecules from that through other nanostructures such as quantum dots, provides an arena for novel quantum transport phenomena [15]. Already the simplest and most intensively studied model of a molecule with a single electronic level and a one-dimensional potential energy surface for the nuclear displacements, gives rise to a plethora of interesting transport regimes such as vibrational sidebands [7, 8], electron shuttles [9], Franck-Condon blockade [10], avalanche-like transport [10], pair tunneling [11], and dynamical symmetry breaking [12]. Generalizations of this model to two electronic levels have been suggested in order to account for nondegenerate but competing molecular states [13] and for degenerate electronic states on a molecular dimer [14].

At first sight, one may think that extensions to higher-dimensional potential energy surfaces are straightforward and do not yield qualitatively new effects. This expectation, however, is disappointed for molecules with symmetry-induced degeneracies of both electronic and vibrational states. Under these conditions, the Jahn-Teller effect [16] can lead to nontrivial vibrational dynamics, originating from conical intersections of the adiabatic potentials with their associated geometric (Berry) phases. In transport, one expects to be particularly sensitive to this intriguing dynamics when the tunneling of electrons between molecule and leads switches the molecule between a symmetric and a Jahn-Teller distorted charge state.

In this paper, we investigate the consequences of this Berry phase on transport through single Jahn-Teller molecules. We focus on the $E\otimes e$ Jahn-Teller effect, which occurs in a large variety of triangular (X_3), tetrahedral (ML_4—a transition metal ion M surrounded by a tetrahedron of ligands L), and octahedral molecules ML_6. We show that the Berry phase induces a nontrivial selection rule for transitions between molecular charge states. In combination with the energy spectrum of the Jahn-Teller molecule, this leads to the formation of trapping states with characteristic consequences for the transport properties of Jahn-Teller molecules such as asymmetry of the current-voltage characteristics and strong negative differential conductance (NDC).

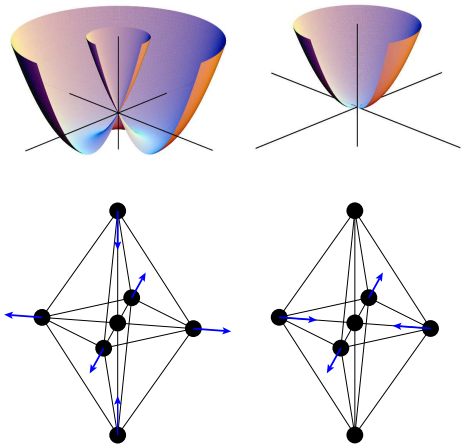

FIG. 1: **Top:** Adiabatic potentials of the $E\otimes e$ Jahn-Teller distorted (charged) molecule (left) and the undistorted (neutral) molecule (right) as a function of $(Q_\theta, Q_\varepsilon)$. **Bottom:** Displacement patterns of the degenerate θ and ε vibrations for octahedral ML_6 molecules.

Jahn-Teller molecule.—Molecules exhibiting the $E\otimes e$ Jahn-Teller effect are characterized by two degenerate electronic states coupled to two degenerate vibrational modes θ and ε. In the case of an octahedral ML_6-molecule, the relevant electronic states are of $d_{x^2-y^2}$- and $d_{3z^2-r^2}$-type, and the degenerate vibrations correspond to the symmetric oscillations of the ligands indicated in Fig 1. For definiteness, we assume that the degenerate electronic E states are empty in the neutral molecule and filled with one electron in the charged state [21]. With

this choice, the molecular Hamiltonian is [16]

$$H_{E\otimes e} = V_g n_d + \frac{\hbar\omega}{2}(P_\theta^2 + Q_\theta^2 + P_\varepsilon^2 + Q_\varepsilon^2) + \sqrt{2}V_E\hbar\omega\,(Q_\theta\sigma_x + Q_\varepsilon\sigma_y)\,n_d. \quad (1)$$

We use a pseudospin notation with Pauli matrices σ_i for the electronic states $|+\rangle$, $|-\rangle$. The dimensionless strength of the linear coupling of electronic and vibrational degrees of freedom is denoted by V_E, and ω is the frequency of the vibrational mode with effective mass M and oscillator length $\ell_{\rm osc} = (\hbar/M\omega)^{1/2}$. The dimensionless coordinates Q and momenta P of the normal modes θ and ϵ are measured in units of $\ell_{\rm osc}$. The gate voltage V_g tunes the energy of the degenerate electronic levels. Electronic occupations different from $n_d = 0$ (neutral molecule) and $n_d = 1$ (charged molecule) are effectively projected out by assuming a large charging energy U.

Berry phase and selection rule.—Some intuition into transport through Jahn-Teller molecules can be gained by inspection of the adiabatic potential surfaces (see Fig. 1). These are obtained by diagonalizing the electronic part of the Hamiltonian (1) for fixed normal mode coordinates. For the charged Jahn-Teller molecule, one finds the adiabatic eigenstates $|\pm\rangle_{\rm ad} = 1/\sqrt{2}\big(e^{i\varphi/2}\,|+\rangle \pm e^{-i\varphi/2}\,|-\rangle\big)$ and a characteristic "mexican hat" potential surface, which exhibits a minimum at finite distortion. (Here, φ denotes the azimuthal angle in the (Q_θ, Q_ϵ)-plane.) The corresponding potential surface of the neutral molecule is just the two-dimensional harmonic oscillator potential.

The potential surfaces of both the neutral and the charged molecule are $U(1)$ symmetric in the space spanned by the degenerate normal modes (Q_θ, Q_ϵ), seemingly implying that tunneling conserves the corresponding pseudo-angular-momentum quantum number. However, a crucial difference between the two adiabatic potentials is the conical intersection of the two sheets of the adiabatic potential in the charged state. Along any loop enclosing the conical intersection, the electronic pseudospin of the adiabatic eigenstates rotates by 2π [17]. As a consequence, the adiabatic eigenstates acquire a Berry phase of π along such closed loops, which must be offset by the vibrational wavefunction in order to make the full (electronic plus vibrational) wavefunction single-valued. This implies *anti*periodic boundary conditions for the vibrational wavefunction and thus *half-integer* pseudo-angular momenta.

Thus, tunneling of electrons onto or off the molecule switches the pseudo-angular momentum between integer and half-integer values l and j, and strict angular momentum conservation is replaced by the selection rule $l = j \pm \frac{1}{2}$. Indeed, the rate for tunneling onto or off the molecule contains the overlap of the wavefunction of the neutral molecule $\psi_0 \propto e^{il\varphi}$ and of the charged molecule

$$\psi_1 \propto e^{ij\varphi}\,|\pm\rangle_{\rm ad} = \frac{1}{\sqrt{2}}\left(e^{i(j+\frac{1}{2})\varphi}\,|+\rangle \pm e^{i(j-\frac{1}{2})\varphi}\,|-\rangle\right). \quad (2)$$

The overlap $\langle\psi_1|\psi_0\rangle$ vanishes unless $l = j \pm \frac{1}{2}$. Although this derivation of the selection rule is based on the adiabatic approximation, the result remains valid in a full quantum treatment in terms of Franck-Condon matrix elements, as it is shown below.

Transport.—We consider an $E\otimes e$ Jahn-Teller molecule that is weakly coupled to two Fermi-gas electrodes, $H = H_{E\otimes e} + H_{\rm leads} + H_{\rm mix}$ [8]. Tunneling between molecule and leads is described by $H_{\rm mix} = t_0\sum_{\alpha,\boldsymbol{k},s} c_{\alpha\boldsymbol{k}s}(d^\dagger_{+,s} + d^\dagger_{-,s}) + \text{h.c.}$, where $c_{\alpha\boldsymbol{k}s}$ annihilates an electron with momentum $\mathbf{k}$ and spin s in lead $\alpha = L, R$, and $d_{\pm,s}$ annihilates an electron in the pseudospin state $|\pm\rangle$ on the molecule. Jahn-Teller distortions usually occur on a sub-Ångström scale [16] which is small compared to the scale on which electronic wavefunctions fall off. For this reason, we can neglect the dependence of t_0 on the vibrational coordinates. Including a dependence of t_0 on the electronic states $|\pm\rangle$ would be straightforward, but does not significantly alter our conclusions.

In the weak-coupling regime $T \gg \Gamma$, transport is described by the rate equation

$$\dot{P}^n_q = \sum_{n',q'}\left[P^{n'}_{q'}W^{n'\to n}_{q'\to q} - P^n_q W^{n\to n'}_{q\to q'}\right] + \gamma_{\rm rel} \quad (3)$$

for the occupation probability P^n_q of the molecular eigenstates $|n, q\rangle$ [8]. ($n = 0, 1$ denotes the charge of the molecule, and q is a multiindex for the internal degrees of freedom. Γ is the broadening of the molecular levels due to coupling to the leads.) The tunneling rates are given by Fermi's golden rule, $W^{n\to n'}_{q\to q'} = \frac{2\pi}{\hbar}\rho t_0^2|\langle n'; q'\,|\,d^\dagger_+ + d^\dagger_-\,|\,n; q\rangle|^2\sum_\alpha f_\alpha\big(\Delta E_\alpha(n, n', q, q')\big)$, with the density of states ρ in the electrodes and the Fermi function f_α in lead α. ΔE_α denotes the energy difference of the states in the transition $|n, q\rangle \mapsto |n', q'\rangle$. Finally, $\gamma_{\rm rel} = -(1/\tau)[P^n_q - P^{eq}_q\sum_{q'}P^n_{q'}]$ describes vibrational relaxation towards the thermal equilibrium distribution P^{eq}_q by processes not included in the Hamiltonian such as coupling to the substrate. It is useful to define a time scale τ_0 by the maximal tunneling rate $\tau_0^{-1} = 2\pi\rho t_0^2$.

Our results are based on a direct solution of the rate equation (3) *without* recourse to an adiabatic approximation. In this case, the selection rule for pseudo-angular momenta follows from the Franck-Condon matrix elements $\langle n'; q'\,|\,d^\dagger_+ + d^\dagger_-\,|\,n; q\rangle$ between states of the charged and neutral molecule. For the neutral molecule, the eigenstates can be expressed within the angular-momentum eigenbasis of the two-dimensional harmonic oscillator, while for the charged molecule only $j = l + \frac{1}{2}\sigma$ is a good quantum number. Thus tunneling onto or off

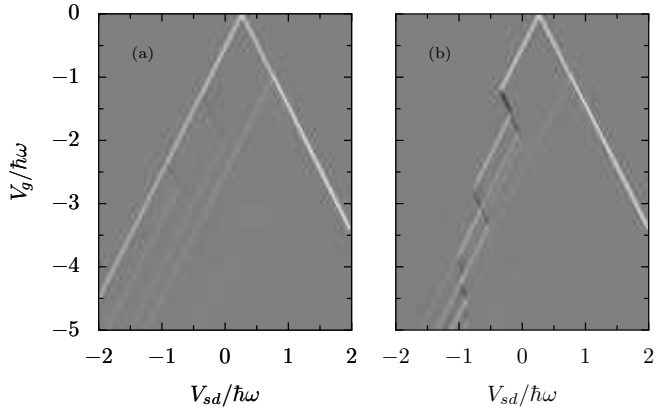

FIG. 2: Differential conductance vs. gate voltage V_g and source-drain voltage V_{sd} for $V_E = 1$, $k_BT = 0.01\,\hbar\omega$. (a) $\tau = 10\,\tau_0$, (b) $\tau = 5000\,\tau_0$. White correspond to positive, dark to negative values.

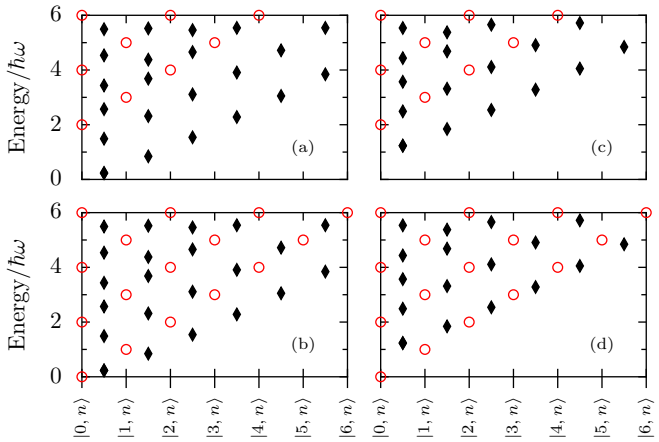

FIG. 3: Angular-momentum resolved spectra of the Jahn-Teller molecule ($V_E = 1$) (diamonds) and the neutral molecule (circles). Radial excitations are grouped for each angular momentum. The spectra of neutral and charged molecule are shifted vertically with respect to each other as described in the text. Panels (a) and (c) show the situation for an electron tunneling onto the molecule, (b) and (d) that for leaving the molecule. The parameters are $V_{\rm sd} = -2\hbar\omega$, $V_g = -0.5\hbar\omega$ ((a) and (b)) and $V_g = 0.5\hbar\omega$ ((c) and (d)).

the molecule changes the pseudo-angular momentum by $\pm\frac{1}{2}$, leading to the selection rule $l = j \pm \frac{1}{2}$ as before.

Results.—The main result of our paper is the differential conductance of a single Jahn-Teller molecule as a function of both bias and gate voltage. The results shown in Fig. 2 for (a) fast and (b) slow vibrational relaxation differ strongly from those obtained for single-mode models [8]. When the molecular orbitals are close to the Fermi energy of the drain electrode (negative V_g in Fig. 2), we find an extended region of current suppression outside the Coulomb-blockaded region, with large negative differential conductance (NDC). No such suppression occurs when the molecular orbitals are close to the chemical potential of the source electrode (positive V_g in Fig. 2), thus rendering dI/dV asymmetric in the gate voltage.

The current suppression can be understood by a trapping mechanism that arises from the interplay of the energy gain due to the Jahn-Teller distortion and the selection rule due to Berry's phase. Representative molecular spectra vs. pseudo-angular momentum are shown in Fig. 3 for various overall vertical shifts between the spectra of the neutral (circles) and the charged (diamonds) molecule. The shifts reflect the energetics of the sequential tunneling processes and are chosen such that tunneling onto the molecule (panels (a) and (c)) occurs only from circles to lower-energy diamonds, while tunneling off the molecule (panels (b) and (d)) is only possible from diamonds to lower-energy circles. In particular, tunneling onto the molecule is possible if

$$\frac{eV_{sd}}{2} + E_{0,l} > V_g + E_{1,j}, \tag{4}$$

where $E_{n,l}$ denotes the vibrational energies of the neutral ($n = 0$) and the charged ($n = 1$) molecule. Correspondingly, the vibrational energies of the charged molecule in panels (a) and (c) have been shifted relative to the neutral molecule by $-(V_g - eV_{sd}/2)$. Tunneling off the molecule if allowed when

$$V_g + E_{1,j} > E_{0,l} - \frac{eV_{sd}}{2}. \tag{5}$$

The analogous shift in panels (b) and (d) is $-(V_g + eV_{sd}/2)$.

One feature of the spectra in Fig. 3 that is crucial for the trapping mechanism is that with increasing pseudo-angular momentum, the lowest state of the Jahn-Teller distorted molecule shifts to lower energies relative to the symmetric neutral molecule. We first focus on the situation when the molecular orbitals are close to the Fermi energy of the drain, where we find the additional suppression of the conductance (see the corresponding spectra for $V_{\rm sd} = -2\,\hbar\omega$ and $V_g = -0.5\,\hbar\omega$ in Figs. 3 (a) and (b)). The angular-momentum selection rule implies that tunneling only takes place between states in *neighboring* columns of Fig. 3. For tunneling onto the molecule (panel (a)), we always find a lower-lying diamond, irrespective of the initial vibrational state of the neutral molecule (circle). In contrast, when tunneling off the molecule (panel (b)), there are initial states of the charged molecule (diamonds) that are below any vibrational state of the neutral molecule that is accessible by the angular momentum selection rule, namely all lowest-energy states with pseudo-angular momentum $\geq 3/2$ in Fig. 3(b). Once the system has fallen into such a state by tunneling onto the molecule, tunneling off the molecule is prohibited and the electron is therefore *trapped*. This trapping effect leads to the current suppression when the molecular orbitals are close to the Fermi energy of the drain electrode.

The above considerations apply strictly only in the absence of additional vibrational relaxation processes that are not induced by tunneling electrons ($\gamma_{\rm rel} = 0$). The trapping and hence the current suppression are clearly weakened by vibrational relaxation. Indeed, the trapping induced features in the differential conductance in Fig. 2 weaken as the phenomenological vibrational relaxation rate $\gamma_{\rm rel}$ is increased. Nevertheless, the two panels of Fig. 2 show that most of the non-equilibrium features in (b) qualitatively survive for the larger value of $\gamma_{\rm rel}$ in (a).

It is now clear why no such trapping effect and hence no current suppression can occur when the molecular orbitals are close to the Fermi energy of the source electrode. This situation ($V_{\rm sd} = -2\,\hbar\omega$ and $V_g = 0.5\,\hbar\omega$) is shown in Figs. 3 (c) and (d) for tunneling onto and off the molecule, respectively. Indeed, there are energetically allowed transitions consistent with the selection rule for any initial state. Fig. 3 thus explains the asymmetry of dI/dV with respect to the gate-voltage.

More quantitatively, Eqs. (4) and (5) combined with the vibrational spectra can be applied to predict the positions of the various lines generated by the trapping mechanism in the differential conductance vs. bias and gate voltage [18]. In addition, it is evident from Fig. 2 that there are regions where for fixed gate voltage the system is in the Coulomb blockade at small source-drain voltages, it is conducting (no Coulomb blockade) at intermediate voltages, and blockaded again at yet higher bias due to the trapping mechanism described above. Thus, the trapping mechanism induces strong *negative differential conductance*, which may indeed be one of its principal experimental hallmarks.

Electric field.—We finally discuss several experimental issues. Placing a Jahn-Teller molecule between two biased electrodes exposes it to a potentially large electric field. For a semiconductor quantum dot, weak coupling and good screening implies that the potential drop is concentrated in the contact regions between the electrodes and the dot. For a single molecule, however, this is less obvious. Thus, the electric field may lift the electronic degeneracy by the Stark effect and mix the vibronic levels by breaking the rotational symmetry of the adiabatic potential.

To estimate the mixing of vibronic levels, we note that the relevant vibrational modes $|\theta\rangle$ and $|\varepsilon\rangle$ do not possess a dipole moment and are therefore unaffected by the electric field unless anharmonic mode mixing becomes relevant when other, "dipole-active" modes are strongly displaced. However, one readily estimates for relevant electric fields (corresponding to voltage drops of the order of $\hbar\omega$) that typical displacements of dipole-active vibrational modes are small compared to their oscillator length $\ell_{\rm osc}$, so that no anharmonic effects are expected. Assuming that the dipole moment is of order ex, where x is the displacement of the dipole-active mode, we obtain a displacement $x \sim eE/M\omega^2 \sim \ell_{\rm osc}^2/d \ll \ell_{\rm osc}$. Here, d is a length of the order of the size of the molecular junction. Similarly, we note that the electric field does not directly couple the two electronic levels as both are d orbitals. The Stark shift is therefore quadratic in the electric field, and we estimate that it is several orders of magnitude smaller than the vibrational frequency.

The phenomenological vibrational relaxation rate $\gamma_{\rm rel}$ is difficult to estimate. However, several experiments on single-molecule junctions have provided strong evidence that the molecular vibrations have been driven far out of thermal equilibrium [19, 20].

Conclusions.—We have shown that symmetry-induced degeneracies of electronic and vibrational modes can lead to new transport phenomena in single-molecule junctions. When the molecular junction consists of, say, an octahedral complex with an $E\otimes e$ Jahn-Teller effect, a combination of Berry-phase effects and a spectral trapping mechanism results in a non-trivial current blockade, even for parameters where the Coulomb blockade is lifted. It is evident from the understanding of this blockade mechanism developed in this paper that it is associated with strongly enhanced shot noise of the current [18]. An interesting open question concerns the effects of nonabelian "Berry phases" on transport in systems with more complicated Jahn-Teller effects.

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