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Quantum Electronic Transport in a Configuration Interaction Basis

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ABSTRACT: An overview of a many-body approach to calculation of electronic transport in molecular systems is given. The physics required to describe electronic transport through a molecule at the many-body level, without relying on commonly made assumptions such as the Landauer formalism or linear response theory, is discussed. Physically, our method relies on the incorporation of scattering boundary conditions into a many-body wavefunction and application of the maximum entropy principle to the transport region. Mathematically, this simple physical model translates into a constrained nonlinear optimization problem. A strategy for solving the constrained optimization problem is given. © 2004 Wiley Periodicals, Inc. Int J Quantum Chem 100: 1163–1169, 2004

Key words: configuration interaction basis; many-body approach; maximum-entropy principle; quantum electronic transport; scattering-boundary conditions

Introduction

Measurement and theoretical prediction of current-voltage (IV) characteristics for molecular-scale electronic devices remains a challenge. Pronounced quantum mechanical effects are expected to be increasingly important technologically in upcoming years as the minimum feature size of transistors in integrated circuits approaches molecular scale dimensions. There are ab initio approaches [1, 2] that have been constructed for calculating these IV relationships for molecular-scale systems, and several assumptions and approximations are typically relied upon:

- electronic structure calculation using density functional theory (DFT) in the local density approximation (LDA) or generalized gradient approximation (GGA) and use of the Kohn-Sham eigenstates as “physical” single-particle states;
- treatment of the applied voltage bias $V$ such that its main effect is to raise the electron energies on the left contact above those on the right by an amount $eV$ and the assumption that only the states within the bias window (difference in potential between left and right contacts) contribute to the transport.© 2004 Wiley Periodicals, Inc.
contacts) are those contributing to the electric current;

- application of the Landauer–Büttiker formalism to derive conductivities from the transmission and reflection coefficients of the resulting one-electron wavefunctions;
- physical current is determined from the off-diagonal matrix elements of the one-body density matrix—there is no formal means of obtaining the one-body density matrix from DFT calculations, and hence no method exists for calculation of current density outside of current DFT (where a given current density is assumed).

Transport calculations based on DFT have been applied to calculate IV characteristics and are useful as estimates if electron correlation is unimportant; however, they generally predict currents two to three orders of magnitude larger than those experimentally observed [3, 4]. It is not known if the discrepancies are due to experimental uncertainties in measurements of the IV characteristics for a single molecule or if they are due to the different approximations made in constructing theoretical models. However, discrepancies between the predictions made from differing theoretical treatments indicate that aspects of the fundamental physics behind electronic transport are not completely understood. Clearly, from a technological viewpoint, it is important to know the correct order of magnitude of current flowing through a nanoscale device, and it is essential from an information design perspective that consistent and accurate representations of IV characteristics for molecular scale systems become available. For molecular and solid-state calculations of electronic structure, there is a large body of knowledge on the effects of various approximations made within a model chemistry. For example, starting from the Hartee–Fock approximation, systematic treatments such as perturbation theory, coupled cluster theory, and configuration interaction (CI) are available to study the approximations being made from a less accurate theoretical treatment. For DFT, treatment of the error due to various approximations is less systematic, but nonetheless a large body of calculations exists and can be compared between differing theoretical treatments and experiment. There is not a comparable body of knowledge for the calculation of electronic structure for transport (open-boundary condition) problems.

A physical scheme for transport at the many-body level and its implementation leading to calculation of IV curves for molecular-scale systems is presented. The approach taken is akin to the standard quantum chemistry philosophy that the most accurate treatment available should be applied to a problem and that systematic approximations then be derived from this higher-level theoretical treatment. With this spirit in mind, open-boundary conditions are applied to a many-body wavefunction calculated by the CI technique. This approach is intended to remove as many approximations from the calculation of the current carrying many-body wavefunction as possible, and to allow for a systematic treatment of electron correlation. This effect of electron correlation on molecular properties is well documented, and there is a very reasonable expectation, if not a certainty, that correlation effects play an important part in the transport problem.

**Method Description**

The idea behind our quantum many-body transport method is to calculate the electronic wavefunction for a contact-molecule-contact system with applied voltage, which minimizes the electronic energy on the transport region subject to contact regions being described as electron reservoirs. The application of scattering-boundary conditions to model electron reservoirs is well known, but a form of these open-system-boundary conditions suitable for many-body wavefunctions has only recently been proposed [5]. The difficulty arises in that the conventional form of the scattering-boundary conditions to model electron reservoirs is well known, but a form of these open-system-boundary conditions suitable for many-body wavefunctions has only recently been proposed [5]. The difficulty arises in that the conventional form of the scattering-boundary conditions to model electron reservoirs is well known, but a form of these open-system-boundary conditions suitable for many-body wavefunctions has only recently been proposed [5]. The difficulty arises in that the conventional form of the scattering-boundary conditions to model electron reservoirs is well known, but a form of these open-system-boundary conditions suitable for many-body wavefunctions has only recently been proposed [5].

The two metal contacts bonded to the molecule are taken to act as electron reservoirs. When a molecule is placed in the gap between two contacts (e.g., as in a typical break-junction experiment) electrons from the left contact can flow through the molecule to the right contact, giving rise to a net electric current. It is postulated the electron distri-
quantum electronic transport

functions of momentum or position, Wigner [9] allows. For a portrait of the electronic motion described by the Hamiltonian and of the many-body wavefunction, as several conceptual issues arise:

- What is meant by incoming electrons on the left (or right)? All electrons are indistinguishable, and there is no localization of a single electron beyond the one-body density \( \rho(\mathbf{r}) \), yielding the probability of finding any electron at position \( \mathbf{r} \).
- How is transmission defined for a single electron in a many-body wave function?
- What is meant by single particle energies, single-particle distribution functions, and Fermi levels for an interacting many-body system?

Formulation and application of the scattering-boundary conditions for many-body wavefunctions in our approach relies on the use of the Wigner function \( f(\mathbf{q}, \mathbf{p}) \) and resolves the conceptual difficulties listed. The Wigner function has been previously used to apply scattering-boundary conditions to single-particle quantum transport through heterostructures such as resonant tunneling diodes [6–8].

The first-order Wigner function \( f(\mathbf{q}, \mathbf{p}) \) of an \( N \)-electron wavefunction \( \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) \) is defined by

\[
f(\mathbf{q}, \mathbf{p}) = N \int e^{-i\mathbf{p}\cdot\mathbf{r}} \Psi^* (\mathbf{q} - \mathbf{r}/2, \mathbf{r}_2, \ldots, \mathbf{r}_N) \times \Psi (\mathbf{q} + \mathbf{r}/2, \mathbf{r}_2, \ldots, \mathbf{r}_N) d\mathbf{r}_2 \ldots d\mathbf{r}_N \quad (1)
\]

where atomic units (\( h = m_e = e = 1 \)) are used. It is a real function, with \( \mathbf{q} \) interpreted as position and \( \mathbf{p} \) as momentum and yields as much of a phase–space portrait of the electronic motion described by \( \Psi \) as the Heisenberg uncertainty principle allows. For functions of momentum or position, Wigner [9] showed that the expectation value in \( \Psi \) can be calculated simply by interpreting \( f(\mathbf{q}, \mathbf{p}) \) as a probability density for the system to have momentum \( \mathbf{p} \) at position \( \mathbf{q} \). For example, the kinetic energy is given by

\[
\langle \Psi | T | \Psi \rangle = \frac{1}{(2\pi)^{3N}} \int \frac{\mathbf{p}^2}{2} f(\mathbf{q}, \mathbf{p}) d\mathbf{q} d\mathbf{p} \quad (2)
\]

and similarly for a one-electron operator such as the nuclear potential \( V(\mathbf{q}) \). Note that expectation values of two-electron operators such as the electron–electron interaction can be calculated using the second-order Wigner function \( f(\mathbf{q}_1, \mathbf{q}_2, \mathbf{p}_1, \mathbf{p}_2) \), and so forth for \( N \)-body quantities. The uncertainty principle states that the position and momentum of a particle cannot be known simultaneously. Thus, the function \( f \) cannot be expected to have all the properties of a classical probability density: some features of the function violate a classical interpretation due to quantum effects. Most notably, the Wigner function \( f \) need not always be positive, as is strictly required for a probability distribution function. However, the Wigner function is known to provide a useful, although not unique, phase–space portrait of quantum mechanics. The Wigner function has been used [6] to implement the scattering-boundary conditions for one-dimensional, noncorrelated electrons. For the reservoir picture, it is essential to identify incoming electrons from the left and right in the many-body wavefunction \( \Psi \), and with the aid of the Wigner function this becomes a straightforward process. Consider a plane perpendicular to the current flow chosen to be situated in the left contact. The Wigner function for \( p_z > 0 \) is computed for the incoming electrons located at any point on this plane. To simplify the analysis, we integrate this quantity over the in-plane coordinates; with this function the net inward momentum flow from the left contact is specified. The Wigner function is computed from the initial equilibrium (no applied voltage) wavefunction and evaluated for a chosen number of momenta values \( p_z > 0 \). A similar procedure for the right contact is followed, with the distinction that the electrons incoming from the right are those with \( p_z < 0 \).

To be explicit, a description of the form of the Hamiltonian and of the many-body wavefunction used to describe the transport region is given. The Hamiltonian operator is the nonrelativistic N-electron Coulomb Hamiltonian and is given by
\[ \hat{H}_0 = -\sum_{i=1,N} \frac{1}{2} \nabla_i^2 + \sum_{i=1,N} U(r_i) + \sum_{1\leq i<j\leq N} \frac{1}{|r_i - r_j|}, \]  

(3)

with \( U(r) \) the attractive potential energy of an electron in the Coulomb field of the atomic nuclei. The wavefunction for the \( N \)-electron system is represented by a CI expansion [10] and is written as a sum of spin-projected Slater determinants \( \Psi_\mu \) (also known as configuration state functions, or CSFs). The CSFs used are built from real molecular orbitals, hence, the CI expansion coefficients \( c_\mu \) are chosen to be complex numbers to allow the expansion to describe many-body current carrying states

\[ \Psi = c_1 \Psi_1 + c_2 \Psi_2 + \ldots . \]  

(4)

Any many-body wavefunction can be written as an infinite sum of Slater determinants [11], and this method in principle deliver the exact solution of the many-body Schrödinger equation. The usefulness of CI is that truncated sums of well-chosen CSFs can give accurate results for any electronic property with a controllable approximation to the electron correlation energy, namely, the length of the CI expansion. All that needs to be specified for a CI calculation is a set of expansion functions for the description of the single-electron orbitals and the occupations for the finite set of CSFs used in the CI expansion. The CI method proceeds to find the ground and excited states of a quantum system by obtaining stationary points of the energy \( \langle \Psi | \hat{H} | \Psi \rangle \) while preserving the normalization constraint \( \langle \Psi | \Psi \rangle = 1 \). In practice, the set of CSFs to be selected for an accurate description of the problem is crucial for a successful treatment of a correlated problem: the Monte Carlo configuration interaction [12, 13] has been used to determine the CI vector expansion. With this approach, a CI vector is generated and random single and double substitutions are made with respect to this trial vector. The problem is solved with the expanded vector, and then configurations that contribute significantly to the wavefunction are retained. The procedure is iterated until the calculation converges. Note that the method always works with a compact CI vector, is not excitation-limited, and inherently has importance sampling of the CSF space built-in, as only those excitations accessible via single and double substitutions relative to the trial vector are accessible. This last fact implies that the algorithm always works with a substantially reduced CI space and yet can recover any portion of the correlation energy desired by lowering the acceptance criterion for CSFs.

The CI variational problem is typically solved through an associated eigenvalue problem: \( \hat{H} \) is projected into the basis of the \( \Psi_\mu \) the resulting matrix \( H_{\mu\nu} \) is then numerically diagonalized. However, in the current formulation additional constraints—those arising from imposition of the scattering boundary conditions—are required, and there is no associated linear eigenvalue problem. Another means for approaching the variational formulation is needed. The many-body wavefunction for the current-carrying state induced by the applied electric field \( \xi \) and satisfying the reservoir boundary conditions is solved for by treating the variational problem as a constrained minimization problem. The steps required are the minimization of the energy \( E = \langle \Psi | \hat{H}_0 + \xi \xi^* | \Psi \rangle \) subject to the normalization and Wigner boundary constraints, \( \langle \Psi | \Psi \rangle = 1 \) and \( \langle \Psi | \hat{F} | \Psi \rangle = f \), respectively.

The constraints require that the values for the Wigner function calculated from the minimizing wavefunction match those calculated from the equilibrium wavefunction at the points in Wigner phase space chosen to model the behavior of the electron reservoirs. Note the outgoing electrons on the left or on the right contacts are not constrained: the molecule is free to choose to reflect or transmit as many electrons as needed to minimize the constrained energy. Once the constrained minimization problem is solved, resulting in a minimizing wavefunction \( \Psi \), the current is calculated from the probability current density \( J(r) \). The current density for the many-body case can be compactly expressed using the one-body density matrix as

\[ J(r) = \frac{1}{2i} \langle \nabla_\rho(r', r) - \nabla_\rho(r, r') \rangle_{r=r'}. \]  

(5)

This current density is integrated over the plane normal to the net flow to obtain the total electron current passing through the molecule.

The formulation of the constraint problem reveals that the minimization function involved is nonlinear, as \( \Psi \) enters at least quadratically within the many-body expectation values. Unconstrained nonlinear optimization problems may be solved by a variety of methods: steepest descent, conjugate gradients, Newton’s method, quasi-Newton methods, etc. The presence of the additional constraints makes the minimization problem difficult. Most algorithms for solving nonlinearly constrained, non-
linear problems attempt to solve iteratively a sequence of related unconstrained problems, using the methods listed above. For the quantum many-body transport problem as formulated in this paper, a well-established iterative procedure, the Lagrange multiplier penalty function method [14, 15], is applied. An augmented Lagrangian $\mathcal{L}$ is defined:

$$
\mathcal{L}(\Psi, \lambda, \sigma) = \langle \Psi | H + \epsilon z | \Psi \rangle - \sum_{i=1}^{n} \lambda_i c_i(\Psi) + \frac{1}{2} \sigma \sum_{i=1}^{n} c_i^2(\Psi), \quad (6)
$$

with the first term the unconstrained energy (with application of an external electric field), the second term is the sum of constraint violations with their respective Lagrangian multipliers $\lambda_i$, and the third term is the penalty term added directly to the Lagrangian. The Lagrange multiplier penalty function method has the advantage of relatively quick convergence, quicker, for example, than simple penalty function methods. It can also be shown that this eliminates ill-conditioning problems associated with direct use of penalty function terms. Details may be found in Refs. [14–16].

Finally, as a technical aside, we note that the use of nonlocal effective core potentials (ECPs) or pseudopotentials has implications for the current from electronic structure calculations. Nonlocal potentials such as pseudopotentials or ECPs do not carry a constant current: the continuity equation

$$
\nabla \cdot \mathbf{j}(\mathbf{r}) + \frac{\partial \rho}{\partial t} (\mathbf{r}) = 0 \quad (7)
$$

derived from the Schrödinger equation with a local potential $V(\mathbf{r})$ does not hold for nonlocal potentials. Although the scattering phase-shifts of the pseudopotential may be correct, yielding the transmission coefficient for the complete molecular structure, the current that passes through core regions of the molecule will not be constant. In our representative calculations, the current is averaged only over the molecule where ECPs have not been used. This effect arising from the use of nonlocal effective potentials should be present for all molecular electronics calculations using the pseudopotential/ECP approximation, and this fact seems to have escaped notice in the literature to date. To address this problem, a constant-current constraint was allowed to be included in the minimization procedure, in addition to the Wigner function constraints capturing the scattering-boundary conditions. Continuity-violating currents can also be a result of the approximate solution to the wavefunction: due to either the finite set of single-electron molecular orbitals used or the finite set of CSFs selected for the CI calculation. The constant-current constraint forces the minimizing wavefunction to have a constant-current crossing a number of planes, specified by giving a grid in the direction of current flow. However, the test calculations to date have not used ECPs on the phenyl component of the system, and the current across the molecular system has been constant within numerical errors. The formalism as described above is not changed in the presence of constant-current constraints: they are included in constraint conditions, and no additional modification to the computations is required.

**Results**

Details of current-voltage characteristics for the benzene–dithiol molecule bonded between two gold clusters have been computed using the approach described [5]. In our previous work, the IV characteristics for benzene–dithiol computed as a singlet state was considered. One of the advantages of the formulation presented is that exact-spin eigenfunctions are determined, and further calculations are presented to confirm that the IV characteristic described for the singlet state indeed remains the current carrying ground state as a voltage is applied. In Figure 1, the ground state and first few excited states have been calculated for the gold–benzene dithiol–gold complex. Within the figure, the lowest-energy singlet state at zero electric field is shown as it evolves under application of voltage as a bold line. In addition, an excited singlet state that crosses the ground state near 2.5 V is also displayed in bold. As reported previously, these singlet states are the states that couple to the applied electric field, and the current resonance observed corresponds to the curve crossing near 2.5 V, where substantial excited-state character mixes into the ground state. Resonant electronic transport is observed at voltages above the curve crossing. Other singlet states are displayed in Figure 1 as solid lines. Additionally in the figure, the dashed lines are the low-lying triplet excitations of the complex, and these remain energetically well above the singlet ground state for all voltages considered. For
higher temperatures, weighting of excited states through a statistical density matrix is required, but it is noted that the large energy difference calculated indicates that the triplet mixing is minimal for the voltages and temperatures typically considered in the molecular transport problem. It is observed that below the curve crossing that the induced dipole moment of the complex results in an increase in the complex’s dipole moment as \( p = a\alpha \), with \( \alpha \) the system polarizability. At resonance, a discontinuity in the dipole moment is observed. The singlet excitations polarize and mix under application of the electric field, and at higher fields the charge cloud becomes difficult to polarize, resulting in an approximately fixed dipole moment. This is reflected in the linear decrease in energy of the excited states at larger values of applied voltage. Above the curve crossing, the fixed dipole moment of the complex is a reflection of the mixing of the electronic excitations into the current carrying ground-state wavefunction and is a clear indication of the onset of resonant transport. The computed current is in good agreement with experiment [3]. For example, at 2 V (below resonance), a current of 179 nAmps is computed as compared with the measured value of approximately 60 nAmp. For comparison, DFT methods for the gold–benzene dithiol–gold system predict current magnitudes of 20,000 to 60,000 nAmp at 2 V [17, 18]. Finally, in Figure 2, a plot of the one-body density matrix \( \rho(\mathbf{r}, \mathbf{r}') \) calculated with \( \mathbf{r} = 0 \) and \( \mathbf{r}' \) varied with a bias voltage of \( V = 2 \) V. Within the figure, the real component of the density matrix is seen to correlate along the molecular axis, but that correlation from the center of the molecule into the gold contacts dies off rapidly. The imaginary component of the density matrix is many orders of magnitude lower than the real component, indicating that as voltage is applied, extremely small changes to the wavefunction determine the current magnitude, and this in turn requires an extremely accurate determination of the minimizing wavefunction respecting the Wigner constraints.

**Conclusions**

An overview of a correlated calculation for molecular electronic transport has been given. The method does not rely on the Landauer formalism or other common assumptions used to date in electronic structure theory approaches to transport. The method represents a simple formulation of quantum transport and directly includes many-body effects. The use of the method results in IV charac-

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**Figure 1.** Electronic states in the metal–benzene dithiol–metal complex. The calculation was performed in \( C_{2v} \) symmetry, and only electronic states coupled by a uniform electric field along the molecular axis are shown \((A_1, B_2)\). The thick bold lines display the ground state (originating at 0) and the excited state (originating near 4 eV), which crosses the ground state at approximately 2.5 V. Singlet states are the thinner solid lines; triplet states are the dotted lines.

**Figure 2.** A plot of the real component of the density matrix for \( \mathbf{r} = (0, 0, 0) \) with \( \mathbf{r}' \) varied along the molecular axis calculated at a voltage bias of 2 V.
characteristics in good agreement with experiment, and a clear distinction between resonant and nonresonant transport can be identified through application of the method.

Two features of the approach are of advantage over other common transport formulations. First, conventional electronic device simulations rely on solution of Boltzmann transport equations or various approximations derived from the Boltzmann equation. Central to all these approaches is the determination of the classical electron and hole distributions $f(q, p)$. Clearly, the formulation of the correlated transport problem given above allows for coupling to semiclassical transport simulations by matching boundary conditions $f_{\text{classical}}(q, p) = f_{\text{Wigner}}(q, p)$. As $\hbar \to 0$, $f_{\text{Wigner}} \to f_{\text{classical}}$, and hence the formulation of the quantum transport problem with Wigner boundary conditions allows for natural coupling to classical transport simulations. Second, by working directly with a correlated many-body wavefunction, aspects of the transport problem can be decoupled from issues such as the form of exchange-correlation functionals and other difficult-to-control approximations, and correlation in open systems can be determined. As detailed understanding of the role of electron correlation in transport studies is obtained for small quantum systems, new approximations may be devised for study of transport in larger systems.

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