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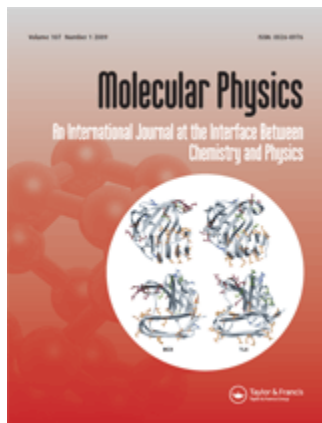
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Electronic current density expanded in natural orbitals

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Quantum electronic currents can be determined directly from off-diagonals of the one electron reduced density matrix. Behaviour of the density matrix in a natural orbital expansion is well understood, whereas very little is known about the current density expressed in any orbital basis. Given the relationship of the current to the density matrix, it seems plausible that improved approximations to the reduced density matrix should lead to better descriptions for the current density. To examine how improved approximations to the reduced density matrix are related to the current density, an upper limit to the error resulting from truncating a natural orbital expansion of the current is found and related to the density matrix and kinetic energy expressed in the same basis. As a consequence, it is confirmed that quantum transport formulations leading to an accurate one-electron reduced density matrix will deliver controllable and well-behaved approximations for quantum electronic currents.

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INTRODUCTION

Recently, substantial effort has been applied to determine electron currents across single molecule tunnel junctions and nanoscale systems. Formal theories for treating non-equilibrium quantum mechanical systems exist [1–4], but there remain unanswered questions as to what level of approximation is needed to treat electron transport across a molecular scale system [5]. Recently it has been pointed out that while for many molecular tunnel junctions commonly applied approaches for treating electronic structure in conjunction with Green's functions and scattering approaches [6] are able to reasonably reproduce experiments in many cases, there remains no systematic means for predicting when these approximate methods fail.

Expansion of the electron density in orbitals to determine ground and excited state properties for many-electron systems has received much attention since the introduction of quantum mechanics. There are also investigations of orbital expansions to accurately represent the one electron reduced density matrix (RDM) [7–9] and, for example,

to determine Compton scattering profiles [10, 11]. However less is known about the expansion of the electronic current density in any orbital basis [12]. It has been shown that electronic correlations can have a deciding role in predicting currents for single molecule tunnel junctions [13]. Recently it has been found numerically that a one-electron density matrix derived from a single Slater determinant with orbitals chosen to maximize overlap to a density matrix obtained from a correlated many-electron state yields currents significantly closer to many-body results for the current, as opposed to calculations using commonly applied criteria for defining single-particle models for systems with open boundary conditions [14]. This finding points to the use of natural orbitals to describe the one-electron reduced density matrix for transport calculations. Although there are indications that they may be derived directly from a single particle Hamiltonian eigenvalue problem [15, 16], in practice they are difficult quantities to obtain *a priori* and in practice are often obtained following an explicitly correlated calculation. Nonetheless natural orbitals are a useful theoretical tool for studying systematic improvement to the RDM, and relating improved approximations to the RDM to the prediction of electronic currents.

The reduced density matrix can be expanded in terms of single electron states

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{j,k=1}^{\infty} n_{jk} \varphi_j(\mathbf{r}) \varphi_k^*(\mathbf{r}'). \quad (1)$$

The states diagonalizing the RDM are natural orbitals (NOs) [17] and their eigenvalues n_k are known as natural occupations. If one asks what is the best finite expansion $\tilde{\rho}$ to the exact RDM in a least squares sense

$$\int |\rho(\mathbf{r}, \mathbf{r}') - \tilde{\rho}(\mathbf{r}, \mathbf{r}')|^2 d\mathbf{r} d\mathbf{r}' = \min, \quad (2)$$

it is found that including the first m natural orbitals with largest occupancies in a truncated expansion expansion

$$\tilde{\rho} \rightarrow \rho_m(\mathbf{r}, \mathbf{r}') = \sum_{k=1}^m n_k \varphi_k(\mathbf{r}) \varphi_k^*(\mathbf{r}') \quad (3)$$

minimizes the error [7–9]. As $m \rightarrow \infty$, the exact one electron reduced density matrix is recovered. In turn, the electronic current density is related to the one electron RDM through a first order differential operator as

$$\mathbf{J}(\mathbf{r}) = \frac{1}{2i} \left[\partial_{\mathbf{r}} - \partial_{\mathbf{r}'} \right] \rho(\mathbf{r}, \mathbf{r}')|_{\mathbf{r}'=\mathbf{r}}, \quad (4)$$

with \mathbf{J} the current density, \mathbf{r}, \mathbf{r}' position vectors, and ρ the one-electron reduced density matrix; atomic units are used. Given the the RDM and current density are related through a differential operator, it is not evident that approximations that improve the RDM in the sense of eq. 2 will necessarily improve the current density, other than as $m \rightarrow \infty$ in which case both the RDM and current density become exact.

There have been a variety of approaches to develop practical quantum mechanical treatments of many-electron systems with open system boundary conditions to determine electron currents across nanoscale systems [18–26] such as quantum dots, nanowires, and single molecule tunnel junctions. Although the specifics of the methods vary, many of these approaches rely on the use of the one-electron Green's function, often in a form that is 0^{th} order in electron correlation, or independent particle form. It is known that improving the treatment of electron correlations with the one-electron Green's function leads to higher order corrections to the reduced density matrix [27]. In this sense, the improvement to the RDM obtained by including correlations to the Green's function can viewed in a similar fashion as increasing the number of expansion terms in the truncated NO expansion given by eq. 3. However, the quantity of interest in transport calculations is the electronic current density as expressed by eq. 4. From an approximate RDM, it is not clear how the current density will behave as the number of expansion terms are increased. In the following, the properties of the electron current density expanded in a NO basis will be studied. In particular, the questions are posed as to whether improving the approximation for the RDM expressed in a truncated NO expansion translates into an improved approximation for the electron current density, and if so, in what form can the improvement be expressed.

NON-LOCAL CURRENT DENSITY

To investigate the physical current density expanded in a natural orbital basis, it is convenient to define a *non-local* current density as

$$\mathcal{J}(\mathbf{r}, \mathbf{r}') = \frac{1}{2i} [\partial_{\mathbf{r}} - \partial_{\mathbf{r}'}] \rho(\mathbf{r}, \mathbf{r}'), \quad (5)$$

with the physical current density obtained from the diagonal terms

$$\mathbf{J}(\mathbf{r}) = \mathcal{J}(\mathbf{r}, \mathbf{r}). \quad (6)$$

The introduction of \mathcal{J} is a shorthand notation for the operator $\frac{1}{2i} [\partial_{\mathbf{r}} - \partial_{\mathbf{r}'}]$ acting on ρ . The physical current density is real $\mathbf{J} \in \mathbb{R}$, whereas in general for off-diagonal $\mathcal{J} \in \mathbb{C}$. The non-local current density in the natural orbital expansion is given by

$$\mathcal{J}(\mathbf{r}, \mathbf{r}') = \frac{1}{2i} \sum_{k=1}^{\infty} n_k [\varphi_k^*(\mathbf{r}') \partial_{\mathbf{r}} \varphi_k(\mathbf{r}) - \varphi_k(\mathbf{r}) \partial_{\mathbf{r}'} \varphi_k^*(\mathbf{r}')]. \quad (7)$$

In analogy to study of the RDM expressed in a NO basis, an error between the non-local current density in a truncated and exact expansion is introduced as

$$\tilde{\epsilon}_m = \text{Tr}(\mathcal{J} - \mathcal{J}_m)^\dagger (\mathcal{J} - \mathcal{J}_m) > 0, \quad (8)$$

with \mathcal{J}_m the non-local current density when calculated using the truncated version to the density matrix eq. 3. Note that $\mathcal{J}^\dagger(\mathbf{r}, \mathbf{r}') = \mathcal{J}(\mathbf{r}', \mathbf{r})$ and likewise $\mathcal{J}_m^\dagger(\mathbf{r}, \mathbf{r}') = \mathcal{J}_m(\mathbf{r}', \mathbf{r})$. The difference between the non-local current density and the approximation \mathcal{J}_m is

$$\Delta\mathcal{J}_m(\mathbf{r}, \mathbf{r}') = \mathcal{J}(\mathbf{r}, \mathbf{r}') - \mathcal{J}_m(\mathbf{r}, \mathbf{r}'), \quad (9)$$

and

$$\begin{aligned} \tilde{\epsilon}_m &= \int d\mathbf{r} d\mathbf{r}' \Delta\mathcal{J}_m(\mathbf{r}', \mathbf{r}) \Delta\mathcal{J}_m(\mathbf{r}, \mathbf{r}') \\ &= -\frac{1}{4} \sum_{j,k=m+1}^{\infty} n_j n_k \left[\langle \varphi_j | \partial_{\mathbf{r}} \varphi_k \rangle \langle \varphi_k | \partial_{\mathbf{r}} \varphi_j \rangle + \langle \partial_{\mathbf{r}} \varphi_j | \varphi_k \rangle \langle \partial_{\mathbf{r}} \varphi_k | \varphi_j \rangle \right] \\ &\quad + \frac{1}{2} \sum_{k=m+1}^{\infty} n_k^2 \langle \partial_{\mathbf{r}} \varphi_k | \partial_{\mathbf{r}} \varphi_k \rangle, \end{aligned} \quad (10)$$

with orthonormality of the orbitals $\langle \varphi_j | \varphi_k \rangle = \delta_{jk}$ assumed.

TRUNCATION ERROR

To proceed, the boundary conditions for the region on which the current density is to be calculated must be specified. For simplicity a rectangular parallelepiped that encloses, for example a molecular wire, is shown in fig. 1. It is assumed the region is large enough that the natural orbitals and current density vanish on the faces parallel to wire axis, and current flow is non-zero only through the faces normal to this axis. The form of the orbitals used to describe the reduced density matrix varies between the regions labelled I, II, and III within fig. 1. On the molecular scattering region III, the electrons are assumed to be correlated such that $\rho^2 \neq \rho$. The voltage across the scattering region is set by the chemical potentials $\mu_L \neq \mu_R$ in the left and right electrodes, respectively with the voltage drop $V = \mu_L - \mu_R$ occurring primarily across the molecular region III. This condition allows the single particle wavefunctions to be expressed in scattering form on the region labelled II. As the electrons propagate deep within the electrodes, shown as region I, they equilibrate through inelastic processes and the asymptotic single electron wavefunctions may be approximated in independent particle form such that $\rho^2 = \rho$. In this case, deep in the left electrode the electrons are

described by a single electron Hamiltonian $\hat{h}_0 + V/2$ whereas deep in the right electrode the electrons are described by $\hat{h}_0 - V/2$; consistent with this picture, charge neutrality in region I is imposed for distances into the electrodes much larger than a mean-free path length [28].

With these conditions, terms in the first summation in eq. 10 can be re-written with the help of an integration by parts:

$$\langle \varphi_j | \partial_{\mathbf{r}} \varphi_k \rangle \langle \varphi_k | \partial_{\mathbf{r}} \varphi_j \rangle = \left[- \langle \partial_{\mathbf{r}} \varphi_j | \varphi_k \rangle + \int d\sigma_{xy} \varphi_j^*(x, y, z) \varphi_k(x, y, z) \Big|_{z=a}^{z=b} \right] \langle \varphi_k | \partial_{\mathbf{r}} \varphi_j \rangle, \quad (11)$$

with $z = a$ and $z = b$ the positions of the planes σ_{xy} defining the boundaries located in the region labelled I. Given the assumptions made for the electrodes regions [28], the surface integral may be evaluated at points in the left and right reservoirs such that the densities $\rho_{kj} = \varphi_j^* \varphi_k$ are equal and the surface terms vanish. The resulting form for the error is

$$\tilde{\epsilon}_m = \frac{1}{2} \sum_{j,k=m+1}^{\infty} n_j n_k |\langle \partial_{\mathbf{r}} \varphi_j | \varphi_k \rangle|^2 + \frac{1}{2} \sum_{j=m+1}^{\infty} n_j^2 \langle \partial_{\mathbf{r}} \varphi_j | \partial_{\mathbf{r}} \varphi_j \rangle \quad (12)$$

In this form, it is clear that all terms in the summations are positive. Therefore, it follows

$$\tilde{\epsilon}_m \leq \tilde{\epsilon}_{m-1}. \quad (13)$$

To obtain a clearer indication of the reduction in the error with increased number of terms in the NO expansion, the following form is useful:

$$\tilde{\epsilon}_m = \frac{1}{2} \sum_{j=m+1}^{\infty} n_j \langle \partial_{\mathbf{r}} \varphi_j | (\Delta \hat{\rho}_m + n_j) | \partial_{\mathbf{r}} \varphi_j \rangle \quad (14)$$

with

$$\Delta \hat{\rho}_m = \hat{\rho} - \hat{\rho}_m = \sum_{k=m+1}^{\infty} n_k |\varphi_k \rangle \langle \varphi_k|. \quad (15)$$

Eq. 14 indicates that the error for the non-local current density as defined is related to truncation errors in the kinetic energy and the RDM expanded in the NO basis. The kinetic energy **converges monotonically in an NO basis as can be seen from**

$$T = \sum_{j=1}^m n_j \langle \partial_{\mathbf{r}} \varphi_j | \partial_{\mathbf{r}} \varphi_j \rangle, \quad (16)$$

as the occupation number and kinetic energy matrix element in each term of the summation are positive. The approximate RDM has minimal least squares error relative to the exact RDM for a set of truncated

1 natural orbitals. Further, given that $0 \leq n_k \leq 1$ and that the magnitude of the truncation error is of order $\mathcal{O}(n^2)$,
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 3 the error decreases rapidly with increasing m for natural orbitals ordered by decreasing occupation number.
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5 To relate the error for the non-local current density to the physical current density, the square of the diagonals are
 6 summed
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$$\begin{aligned} \epsilon_m &= \int d\mathbf{r} d\mathbf{r}' \delta(\mathbf{r} - \mathbf{r}') \Delta\mathcal{J}_m(\mathbf{r}', \mathbf{r}) \Delta\mathcal{J}_m(\mathbf{r}, \mathbf{r}') \\ &= \int d\mathbf{r} |\Delta J(\mathbf{r})|^2. \end{aligned} \quad (17)$$

9
 10 The integrand of eq. 10 is everywhere positive, hence $\epsilon_m \leq \tilde{\epsilon}_m$. In general, it can not be said that the error in the
 11 current density decreases monotonically as the number of NOs in the expansion increases, but the maximum error
 12 given by $\tilde{\epsilon}_m$ does decrease monotonically with increasing m . Finally it is noted that it can be expected that $\epsilon_m \ll \tilde{\epsilon}_m$.
 13 For example, if the error is uniformly distributed over $\{\mathbf{r}, \mathbf{r}'\}$, then $\epsilon_m/\tilde{\epsilon}_m \propto 1/\mathcal{V}$ with \mathcal{V} the volume over which the
 14 current density is calculated.
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28 CONCLUSION

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 30 The error defined for the non-local current density decreases monotonically as the number of natural orbitals in
 31 its expansion is increased. From the explicit expression for $\tilde{\epsilon}_m$, this decrease is related to the errors in the density
 32 matrix and kinetic energy expressed in a truncated NO basis. The physical current density is given by the diagonals
 33 of the non-local current density with $\{\mathbf{r} = \mathbf{r}'\}$. The error measured by $\tilde{\epsilon}_m$ is the sum of the square of the differences
 34 between \mathcal{J}_m and \mathcal{J} across the entire space $\{\mathbf{r}, \mathbf{r}'\}$. Hence the difference between \mathcal{J}_m and \mathcal{J} on the sub-space $\{\mathbf{r} = \mathbf{r}'\}$
 35 is expected to be less than given by $\tilde{\epsilon}_m$, or equal if all the error due to truncating the expansion results directly from
 36 diagonal terms- a condition that there is no reason to expect. The strict monotonic decrease in error shown for the
 37 non-local current density as the number of natural orbitals is increased in a truncated expansion does not guarantee
 38 the error for the physical current density will also monotonically decrease. However $\tilde{\epsilon}_m$ sets an upper limit to the
 39 error for the physical current density.
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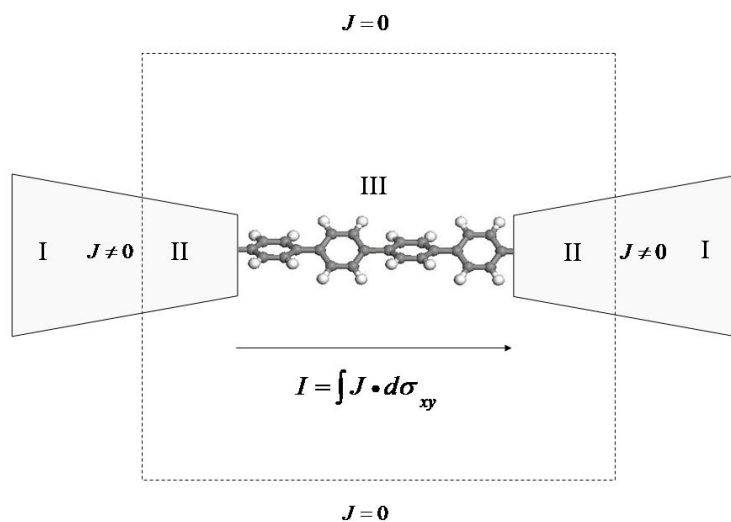
51 As has been previously demonstrated, higher order corrections to the one-electron Green's function lead to improved
 52 approximations to the RDM [27]. This improved density matrix can be compared to the use of a NO expansion,
 53 whereby the least squares error relative to the exact RDM is decreased by including more orbitals into the expansion.
 54 If a current is calculated from this truncated expansion for the density matrix, the squared error relative to the exact
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1 current density is given by $\epsilon_m \leq \tilde{\epsilon}_m$. If the number of NOs in the expansion of the reduced density matrix is increased,
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3 the error in the current density does not necessarily decrease. However, the maximum error given by $\tilde{\epsilon}_m$ will decrease
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5 and this upper limit has been shown to be related to quantities that rapidly decrease as the number of NOs in the
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7 expansion of the density matrix is increased. Although as mentioned in the introduction, it is in principle possible
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9 to obtain NOs from a single particle Hamiltonian, their use in calculations is limited due to theoretical difficulties or
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11 practical issues relating to the need for a full many-particle calculation to determine a NO-set, thus obviating the need
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13 for the orbitals. Hence the results presented here are not a call for the use of natural orbitals in practical calculations
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15 of electron transport. Rather, convergence of the one-electron reduced density matrix can be best examined with the
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17 use of natural orbitals, and calculation of the RDM is well studied. By relating the current density through the use of
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19 a NO-set to the RDM, well-known relationships between correlated treatments of the one-electron Green's function
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21 and the RDM may be apply to the study of the current density. Previously, systematic measures for the error in the
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23 calculation of current densities have not been available.
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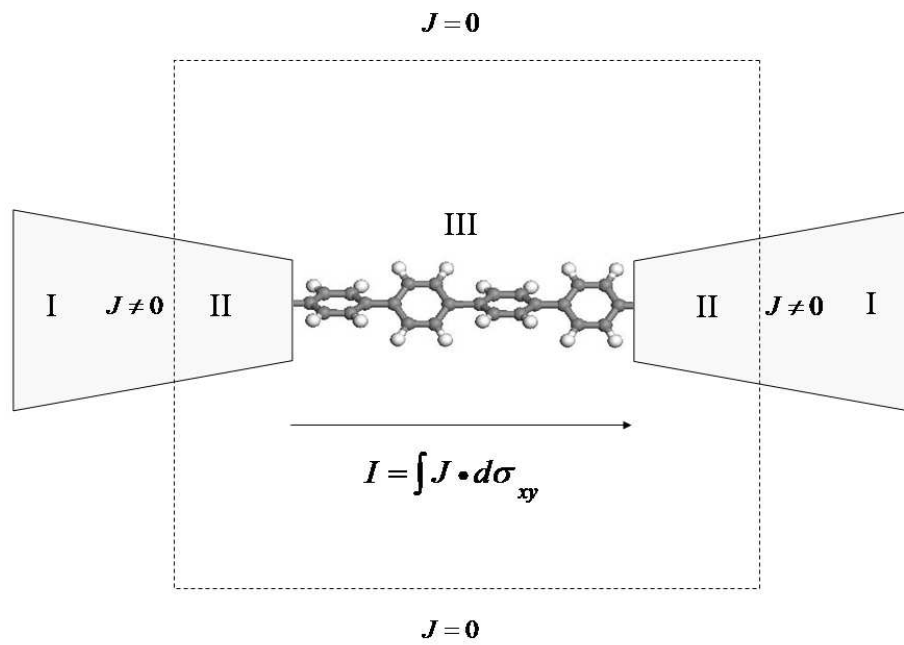
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23 FIG. 1: Cross section for the geometry of a typical molecular tunnel junction. The dashed line represents the volume on which
24 the current density is to be calculated. Current flow is primarily along the molecular axis allowing the choice of a region such
25 that the current density J is zero at the faces of the region situated outside of the electrodes.
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