Electron Transport at the Molecular Scale from First-Principles







Tyndall National Institute





John Tyndall, 1820 - 1893

- Born in Leighlinsbridge, Co.Carlow 1820
- PhD in Marburg, Germany, in 1848, with Robert Bunsen (he of the Bunsen burner)
- Succeeded Faraday as Director of the Royal Institution 1863
- Initiated the practical teaching of science in schools
- Developed infrared spectroscopy
- Invented the light pipe
- Tyndall Scattering explained why the sky is blue
- Tyndallisation sterilisation process
- Studies of the atmosphere and the ozone layer



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Outline



 Background > electric currents at the nanoscale > quantum transport from first-principles
 Many-body formulation Configuration Interaction sources – Wigner distribution boundary conditions sinks – complex absorbing potentials
 Applications > tunnelling currents in molecular wires > correlations & tunnelling transport > evaluation of independent particle approaches



Electric currents at the nanoscale

500 nm

typical problem

S.A. Getty *et al* (Maryland University)

Challenges for the theory:

> physical processes at the interface betweeen small & large

> new effects and device physics due to quantum mechanics, increased complexity and chemical features

electronic structure from first-principles for systems with open boundary conditions



Motivation & Common Approaches





Beyond common approaches

Approximate schemes conceptually and computationally simple	
However, to define their effectiveness and range of validity a method is needed that can yield the exact current-carrying electronic states	
➤ time-dependent DFT	
> perturbation theory, e.g., GW	
configuration interaction	
<u>Our aim</u> : devise transport scheme operating genuinely at the <i>many-body</i> level with	
 precise description of electron-electron interactions inclusion of bulk contacts [(quasi-infinite) wires] 	
www.tyndall.ie	



Many-body formulation: Configuration Interaction

Configuration-Interaction (CI) formalism writing the N-electron system wavefunction as

 $\Psi = \mathbf{c}_1 \mid \mid_1 + \mathbf{c}_2 \mid \mid_2 + \mathbf{c}_3 \mid \mid_3 + \dots$

where $| |_{i}$ = Slater determinant of N single-electron orbitals

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A rough interpretation of many-body physics in Cl







Many-body formulation: Sources





Sources





Problem Definition

What condition should the one-body reduced density matrix fulfil?

Since we are interested in a subsystem we need to

maximise the entropy subject to the system observables

- ➤ energy
- number of particles
- > momentum inflow (our Ansatz)

Semiclassical region f(q,p) Quantum region $\Psi(r_1,r_2,...,r_n)$

low-temperature limit equivalent to minimisation of the total energy $\langle \Psi | \mathbf{H_0} + \mathbf{e} \to \mathbf{x} | \Psi \rangle$ on the device region subject to the "incoming" Wigner distributions constraints $\langle \Psi | \mathbf{f^i} | \Psi \rangle = \mathbf{f^i}$ and $\langle \Psi | \Psi \rangle = 1$

Incoming electrons:

fixed by the nature of the contacts through the momentum distribution f(p)

• Outgoing electrons: fixed by the nature of the device region in an electric field resulting in reflection or transmission of probability, i.e., current,

I = $(\hbar/2im) [\Psi^* \nabla \Psi - \Psi \nabla \Psi^*]$



Computational Scheme

Interface to electronic structure platform Optimised structures with <u>TURBOMOLE</u> code using default atomic basis sets (typically SV(P)) on the DFT mode with B3LYP; take advantage of symmetry (C_{2v}, C_{2h}) SCF calculation in TURBOMOLE with atomic basis of choice extracting molecular orbitals, one- and two- electron integrals Building many-body correlations Monte-Carlo Configuration Interaction (MCCI) or other utility code giving the ground- and excited- state many-body wavefunctions at zero electric field E => converged expansion of many-body wavefunction not necessarily immense Choose the states coupled by the field and perform the constraint minimisation calculation at E yielding the current carrying state for each voltage V



Many-body formulation: Sinks

Absorbing boundary conditions via Self-energy > formally exact > not straight-forward to implement due to single-particle energy dependence

Complex absorbing potentials (CAPs)

formally derived from complex-scaling; however, for practical convenience employ ad hoc local anti-Hermitian operators with negative imaginary part
 absorption of particles through the imaginary wall

> approximate but energy-independent resulting in simple addition of a one-particle operator to the Hamiltonian

> common form chosen to satisfy known constraints and stability conditions or derived from semi-classical approximation

=> requires a search over a parameter space



Self-Energy Transformed Complex Absorbing Potentials (SET-CAPs)

Our approach: exploit relation between self-energy and CAPs

T. Henderson, G. Fagas, E. Hyde, and J.C. Greer,

J. Chem. Phys. **125**, 244104 (2006)



since they both convert a line spectrum (and associated bound states) to a series of resonances just require that they do so in a similar fashion

There are two questions:

- 1. How do we identify the appropriate states and energy levels?
- 2. How do we use those to build the CAP?



SET-CAPs: Construction

Step 1: calculate evolved states of device region as the interaction with reservoirs is adiabatically switched via variation of λ from 0 to 1

$$\left[H_{0} + \lambda \Sigma(\omega_{i}^{\lambda})\right] (U_{i})^{\lambda} = \omega_{i}^{\lambda} (U_{i})^{\lambda}$$

$$\left(V_{i}^{+}\right)^{\lambda} \left[H_{0} + \lambda \Sigma\left(\omega_{i}^{\lambda}\right)\right] = \left(V_{i}^{+}\right)^{\lambda} \omega_{i}^{\lambda}$$

Step 2: accumulating eigenvalues and eigenevectors, it would seem simple to define $\begin{bmatrix} H_0 + W \end{bmatrix} = U \omega V^+$ so that we get the same result as from Σ.

But due to the energy dependence $U V^+$ (or $V^+ U$) $\neq 1$

Hence, approximate

$$\left[H_0 + \overline{W}^{\psi}\right] = U \,\omega \, U^{-1}$$





Self-energy Transformed CAPs: Summary

	Self-Energy	С	CAPs	
Property		Self-energy transformed	Phenomenological	
Energy Dependent	Yes	No	No	
Numerical Optimisation	No	No	Yes	
Extended Device Region	No	No	Yes	
Exact Energy Levels	Yes	Yes	No	
Exact States	Yes	Some	No	
Local	No	No	Yes	



Application: Molecular Tunnel Junctions

basic physics: tunnelling through a barrier





zero-bias tunnel conductance

$$G = G_0 \exp[-2l\sqrt{2\frac{m^*}{\hbar^2}\Phi_b}]$$







Alkanediamines: Comparison to experiment



		Cond	uctance G(ns)	
	NH- anchoring	NH2- anchoring	L. Venkataraman et al, Nano Letters 6, 458 (2006)	F. Chen et al, JACS 128, 15874 (2006)
	2			High-G/LOW-G
		K		
Pentane	34.52±16.51	51.99±24.10	27.12±0.77	-
Hexane	12.96±2.98	30.64± 6.07	11.62±1.16	20.79/1.27
Heptane	4.27±1.03	4.91± 3.26	5.66±1.55	-
Octane	3.65	4.33± 3.26	2.32±2.32	3.85/0.22

G. Fagas and J. C. Greer, Nanotechnology 18, 424010 (2007)

agreement for alkanedithiols is fair but more ambiguous due to Au-S-C anchoring



Tunnel Resistance

treating correlations explicitly

	Alkane-dithiols	Alkane- diamines	Silane-dithiols	Silane- diamines
inverse decay length	0.39Å ⁻¹ (0.5/CH ₂)	0.76Å ⁻¹ (0.98/CH ₂)	0.09 Å ⁻¹ (0.18/SiH ₂)	0.07 Å ⁻¹ (0.14/SiH ₂)
contact resistance	140 kΩ	140 kΩ	900 kΩ	4800kΩ



Complex Band Structure







Alkanediamines:

Comparison to other theoretical results





Silanediamines:

Comparison to other theoretical results





Alkane- and Silane- dithiols: Comparison to Hartree-Fock

	% error relative to including expli	cit correlations
	Alkane-dithiol Silane-dithiol	
inverse decay length	14%	117%
contact resistance	32%	75%

G. Fagas, P. Delaney, and J.C. Greer, Phys. Rev. B 73, 241314(R) (2006)



Correlations: effects beyond that described by a single Slater determinant

Fingerprints via the occupations (eigenvalues) n_i of $\rho(\mathbf{r}, \mathbf{r'})$ in the single-electron basis representations

 $\rho(\mathbf{r},\mathbf{r}')$ [and $\rho(\mathbf{r})$] are calculated from the current carrying Ψ

if $\Psi = \text{Det}[\phi_1(\mathbf{r}_1 \mathbf{s}_1), ..., \phi_N(\mathbf{r}_N \mathbf{s}_N)]$ then N eigenvalues with $\mathbf{n}_i = \mathbf{2}$ (eigenvectors ϕ_i) and all other with $\mathbf{n}_i = \mathbf{0}$

For an observable <X> one may derive an expression for the correlation contributions

using the factorisation properties of reduced density matrices

$$\begin{aligned} &= \sum_{ki} \rho_{ki} X_{ik} = 2/(N-1) \sum_{kij} \Gamma_{kj,ij} X_{ik} \\ &= 2/(N-1) \sum_{kij} [1/2(\rho_{ki}\rho_{jj} - \rho_{kj}\rho_{ji}/2) X_{ik}] + _c \\ _c &= 1/(N-1) \sum_i [n_i(n_i-2)/2] X_{ii} \quad ...use this later for the current \end{aligned}$$

Correlations in Through-bond Tunnelling







Comparison of Correlations between Alkane and Silicon Molecular Wires





Comparison of Independent-particle Models





Why Natural Orbitals? Relation to NEGF

use Hartree-Fock as reference

correct the one-body reduced density matrix to 2nd order

$$ho pprox
ho^{(0)} + \lambda^2
ho^{(2)}$$

equivalent to 2^{nd} order correction in Σ_{ee}

$$[G^{(2)}(\omega)]_{pq}^{-1} = [G^{(0)}(\omega)]_{pq}^{-1} + \Sigma^{(2)}(\omega)_{pq}$$

= $(\omega - \epsilon_p)\delta_{pq} - \frac{1}{2}\sum_{iab}\frac{\langle ab||pi\rangle\langle qi||ab\rangle}{\omega + \epsilon_i - \epsilon_a - \epsilon_b} - \frac{1}{2}\sum_{ija}\frac{\langle ij||pa\rangle\langle qa||ij\rangle}{\omega + \epsilon_a - \epsilon_i - \epsilon_j}$

this improves electron affinities and ionisation potentials and coincides with natural orbitals when $\rho^2 \approx \rho$

R.J. Bartlett, G. Fagas, and J.C. Greer, arXiv:0710.5276



Missing Links



Correlations: Summary

Tyndall		Correlatio Summ
voltage and length d \succ for small voltages => c (i.e., ground state) correla \triangleright at resonance there is qu \triangleright C/C _{max} towards lower v	dependence of correlation: overall constant with increasing field and lations qualitative change to be explored r values with increasing length- system be	same to zero voltage comes least correlated

independent-particle models:

Slater determinant made from natural orbitals with highest occupancy seems to give most of the current contributions

despite weak correlations Hartree-Fock diverges from the many-body values (yielding contradicting results!)

> more important to maximise overlap to many-body wavefunction (or one-body density matrix) rather than to minimise energy with respect to orbitals or density

Challenge? Find an effective equation for natural or Brueckner orbitals

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\left|\left\langle \Phi_{1-\text{det}} \middle| \Psi \right\rangle\right| = \max
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G. Fagas, P. Delaney, and J.C. Greer, Phys. Rev. B 73, 241314(R) (2006)



Concluding Remarks

✓	 Simple, efficient formulation of quantum transport that ➢ explicitly includes many-body effects ➢ allows systematic comparison with other approximate methods
✓	Predicted IV curves in reasonable agreement with experiment for all-studied systems
✓	Distinction between resonant and non-resonant transport needs to be clarified
✓	Independent-particle models and role of correlation are explored
	 overlap to many-body wavefunction criterion for best independent-particle model in off-resonant tunnelling HF with 2nd order correction sufficient
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