

pss header will be provided by the publisher

---

# From A Local Green Function to Molecular Charge Transport

M. Albrecht<sup>1</sup>, A. Schnurpfeil<sup>1</sup>, and G. Cuniberti<sup>2</sup>

<sup>1</sup> Theoretical Chemistry FB08, University of Siegen, 57068 Siegen/Germany

<sup>2</sup> Institute for Theoretical Physics, University of Regensburg, 93040 Regensburg/Germany

Received 15 November 2003, revised 30 November 2003, accepted 2 December 2003

Published online 3 December 2003

**Key words** Green function, incremental scheme, Landauer theory, molecular junctions.

**PACS** 31.25.-v, 31.25.Jf, 73.40.Ns

A local-orbital based *ab initio* approach to obtain the Green function for large heterogeneous systems is developed. First a Green function formalism is introduced based on exact diagonalization. Then the self energy is constructed from an incremental scheme, rendering the procedure feasible, while at the same time physical insight into different local correlation contributions is obtained. Subsequently the Green function is used in the frame of the Landauer theory and the wide band approximation to calculate the electronic transmission coefficient across molecular junctions. The theory is applied to meta- and para-ditholbenzene linked to gold electrodes and various correlation contributions are analyzed.

Copyright line will be provided by the publisher

## 1 Introduction

As of very recently, the trend in miniaturization of electronic devices indicates a possibility to ultimately arrive at electronically active elements being constituted by just a single molecule [1, 2]. Specifically it has been demonstrated in break-junction experiments, that a single organic molecule might be positioned between two electrodes so as to yield what has become known as a molecular junction [3, 4]. Under certain circumstances such a system allows for electron transfer from the one electrode to the other. Based on these experiments two far-reaching conclusions have been ventured, namely that molecular junctions might lead the way to ultimate one-electron switches, and secondly, that such a switch behaviour can be triggered by various rather different physical and chemical circumstances.

However, at present experiments are still notoriously difficult and hard to interpret, thus shifting weight to theoretical considerations which are expected to both create a fundamental understanding of the microscopic processes involved and provide a guidance for improved engineering.

Theoretical descriptions of the problem try to illuminate partial aspects like the role of the molecular electronic structure [5, 6, 7] or the influence of various structural conformations [8, 9, 10]. Some progress has been made recently on certain applications. It is the set of methods based on the local density approximation (LDA) to density functional theory (DFT) as a starting point, which provide numerically affordable applications to the molecular junction problem [5, 6, 7, 8, 9, 10, 11]. LDA-based schemes were pursued by Rakshit *et al.* [11], Pantelides *et al.* [6, 7] and others [5, 8, 9] for carbon wires and benzene-ring-systems. Further approximations are introduced by Gutiérrez *et al.* in an application to an all-carbon-system with nanotubes as electrodes [12]. Along those lines Fagas *et al.* analyzed the off-resonant electron transport in oligomers [13], while both discussed the switch-like behaviour of a  $C_{60}$  ball by means of rotation [12]. Cuniberti *et al.* focused on the role of the contacts at the junction [14, 15]. An application predicting the actual current-voltage behaviour of two aromatic molecules was demonstrated by Heurich *et al.* [16]. A more advanced scheme developed by Xue and Ratner sticks with these approximations, but develops a

pss data will be provided by the publisher

non-equilibrium formalism [17]. An earlier attempt was presented by Wang *et al.* [18]. Further approximations are commonly built on top of LDA, like the tight binding approach (TB) or parameterized minimal basis sets [12]. Another set of approaches renounces completely attempts of *ab initio* calculations and resorts to empirical models [19, 20, 21, 22]. Hettler *et al.* completely abandoned *ab initio* approaches and present a semi-quantitative model in calculations on tunneling transport through benzene [19]. In quite the same spirit, several other groups try to tackle the problem without quantum chemical *ab initio* methods, *e. g.* Ghosh and Datta, who rely on minimal basis set semi-empirical Hückel approaches [20]. An elastic scattering model is introduced by Todorov *et al.* [21]. A broad compilation of models was written by Paulsson *et al.* [22]. In several applications the Kohn-Sham eigenenergies are interpreted as excitation energies which is to a large extent feasible. Principle improvements are available, such as time dependent DFT [23] and the optimized effective potential ansatz [24]. However, it is hard to devise systematically improvable schemes in the frame of DFT.

Wave function based methods, on the other hand, are straightforwardly applicable to both ground state and excited state calculations alike and are amenable to systematic improvement on the numerical accuracy by their very construction. Subsequently, quantities like the DOS or the transport coefficient  $T$  can be obtained in a reliable manner. However, the numerical demand increases tremendously with the system size. Recently it was shown that quantum Monte Carlo techniques (QMC), particularly diffusion Monte Carlo (DMC), can be applied to excited states in solids [25, 26, 27, 28]. A second class of approaches extend the coupled cluster (CC) scheme to excited states. The linear response version of CC was used to obtain excitonic transition energies in  $Be$ ,  $CH^+$ ,  $CO$  and  $H_2O$  [29]. These approaches can be cast into a reformulation which rests on the equation-of-motion (EOM) formalism.

The general bottle-neck of steep increase of numerical effort with system size, however, affects all wave function based methods alike. It is precisely this obstacle which we strive to overcome by a formulation of electron correlations in local orbitals and a hierarchy of correlation contributions called the incremental scheme. In earlier works we performed band structure calculations with wave function based *ab initio* methods [30, 31, 32, 33, 34]. The key enabling such calculations for infinite systems was an approach based on local orbitals and a real space formulation of the self energy.

In the present work this idea is carried over to the case of molecules, with applications to large, heterogeneous systems in mind. The purpose is to display the full theory and introduce the idea of the incremental scheme in order to construct the Green function. We demonstrate that this particular combination of an incremental scheme based on local orbitals and the Green function theory allows for numerical efficiency and generates an analytic tool with local resolution. Once the theory is laid out, the use of the Green function and its underlying incremental scheme is demonstrated in a simplified application to the problem of charge transport across a molecular junction. The junction is thought of as two gold electrodes which are linked via thiol bridges to meta- and para-dithiolbenzene. In Sec. 2 the theory is explained. The numerical results are discussed in Sec. 3 and Sec. 4 contains our conclusions.

## 2 Theory

The Landauer theory used to calculate the transmission coefficient across a molecular junction to be discussed below rests on the calculation of the one-particle Green function for the region between the junctions. Fig. 1 shows a sketch of what we refer to as a molecular junction. It shows an organic molecule between two electrodes, which allow to contact the molecule and measure its current-voltage characteristic. A molecule linked via thiol-bridges to gold electrodes sets a canonical example for such a system.

Recently we implemented a wave function based *ab initio* procedure to set up the Green function for band structure calculations in solids and polymers [32, 33, 34]. Physical insight and numerical efficiency were derived from an incremental scheme in real space [30, 31, 35, 36]. Here we apply similar ideas to the problem of molecular junctions. The calculation of the Green function is described in Sec. 2.1. The

combination of the Green function method with the so called incremental scheme is derived in Sec. 2.2, while Sec. 2.3 depicts the Landauer theory.

## 2.1 The Green function

The starting point of our approach are localized Hartree–Fock (HF) orbitals for the molecular region between the electrodes, which is in the simplest case the bare molecule (cf. below). In terms of such orbitals a model space  $P$  and excitation space  $Q$  are distinguished for the example of virtual states (the case of occupied states being completely analogous) as follows: The model space  $P$  describing the HF level comprises of the  $(N + 1)$ -particle HF determinants  $|\eta\rangle$ , while the correlation space  $Q$  contains single and double excitations  $|\alpha\rangle$  on top of  $|\eta\rangle$ :

$$|\eta\rangle = c_n^\dagger |\Phi_{\text{HF}}\rangle, \quad |\alpha\rangle = c_r^\dagger c_a |\eta\rangle, \quad c_r^\dagger c_s^\dagger c_a c_b |\eta\rangle \quad (1)$$

$$P = \sum_{\eta} |\eta\rangle\langle\eta|, \quad Q = \sum_{\alpha} |\alpha\rangle\langle\alpha|. \quad (2)$$

In this local description indices provide an orbital index  $n$  which is normally taken to indicate a local HF orbital. The idea of locality translates into a restriction of the area the orbital can be chosen from to one or more contiguous spatial parts of the molecule. It is important to note that by enlarging the size of the spatial area thus covered, this approximation can be checked in a systematic way for convergence. A very important implication of this procedure is that the correlation methods employed must be size-consistent. This idea is elaborated upon in Sec. 2.2.

The Green function approach has precisely the merit of being intrinsically size-consistent, so that a diagonalization allows to go beyond perturbative results. Pertaining to the above notation the Green function  $G_{nm}(t) = -i\langle T[c_n(0)c_m^\dagger(t)] \rangle$ , where  $T$  is the time-ordering operator and the brackets denote the average over the exact ground-state, can be obtained from Dyson's equation as:

$$G_{nm}(\omega) = [\omega - F - \Sigma(\omega)]_{nm}^{-1}. \quad (3)$$

Here the self energy  $\Sigma_{kl}(\omega)$  which contains the correlation effects, has been introduced.  $G_{nm}^0(\omega)$  is the HF propagator  $[G^0(\omega)]_{nm}^{-1} = \omega - F_{nm}$ . The correlated energies are given by the poles of the Green function which are numerically iteratively retrieved as the zeros of the denominator in Eq. (3). To construct the self energy the resolvent

$$[\omega - H^R + i0^+]_{\alpha\alpha'}^{-1} \quad (4)$$

is needed. It can be gained from diagonalization of the Hamiltonian

$$[H^R]_{\alpha\alpha'} = \langle\alpha|H - E_0|\alpha'\rangle, \quad (5)$$

where the states  $|\alpha\rangle, |\alpha'\rangle$  are those of the correlation space  $Q$  as in Eq. (1).

Along with a straightforward implementation several perturbative approximations have been derived and analyzed. Theoretical connections to the perturbative effective Hamiltonian [31] were also established.

## 2.2 The incremental scheme

The efficiency of the procedure is derived from the application of an incremental scheme as follows: A sketch of the idea is given in Fig. 2.

As subsets of the incremental scheme some arbitrary spatial parts of a molecule, representing a suitable partitioning, are chosen for this example. An incremental description of the transmission coefficient  $T$  could start with a correlation calculation, in which only excitations inside one of the regions I–VI, *e. g.* region I, are allowed. This results in a contribution to the correlation correction to the self energy, and

ultimately to the transmission coefficient  $T$ . With excitations on top of this being restricted to within region I, the so called one-body increment approximation to the transmission coefficient is obtained from Eq. (10) to be discussed in detail in the next section. Here we just assume, some correlation method to calculate  $T$  would be available. Of course, there are as many one-body increments as regions chosen to map the system. They are thus indexed with the region they are referring to. In a next step the calculation is repeated with excitations correlating the charge carriers being allowed to a region enlarged by one additional part II. The difference with respect to the one-body increment then isolates the effect of additional excitations involving this additional region II and constitutes the two-body increment as shown in Eq. (7). This procedure can be continued to more and more regions. In the end the summation Eq. (9) of all increments is the final approximation to the sought transmission coefficient.

$$\Delta T^I = T^I \quad (6)$$

$$\Delta T^{I,II} = T^{I,II} - \Delta T^I - \Delta T^{II} \quad (7)$$

$$\begin{aligned} \Delta T^{I,II,IV} &= T^{I,II,IV} - \Delta T^{I,II} - \Delta T^{I,IV} - \\ &\quad \Delta T^{II,IV} - \Delta T^I - \Delta T^{II} - \Delta T^{IV} \end{aligned} \quad (8)$$

$$\boxed{T = \begin{aligned} &\sum_{A=I}^{IV} \Delta T^{A,+} \\ &\sum_{A>B=I}^{IV} \Delta T^{A,B,+} \\ &\sum_{A>B>C=I}^{IV} \Delta T^{A,B,C,+} \\ &\dots \end{aligned}} \quad (9)$$

From the experience gained with the incremental scheme in its application to the self energy, a rapid decrease of increments both with the distance between the regions involved and with their number included in the increment can be expected. This means that only a few increments need to be calculated. It is crucial to emphasize that the cutoff thus introduced in the summation Eq. (9) is well controlled, since the decrease of the incremental series can be explicitly monitored.

Furthermore physical information can be extracted from the incremental scheme. In general the relative weight of specific increments with respect to others helps to identify important correlation contributions.

In earlier applications to band structure calculations it was demonstrated that the correlation correction  $\gamma = (LUMO - HOMO)_{HF} - (LUMO - HOMO)_{CORR}$  of the band gap gives a suitable measure of the correlation effects accounted for, where  $(LUMO - HOMO)_{HF}$  is the HOMO-LUMO gap on the HF level and  $(LUMO - HOMO)_{CORR}$  is the correlated result. This correction can also be used as a target quantity for the incremental scheme in very much the same spirit as the transmission coefficient inserted above.

### 2.3 The Landauer Theory

From the Green function, the transport coefficient  $T$  can be straightforwardly obtained in the frame of the Landauer formalism [37]. This theory constitutes an approximation, assuming zero voltage across the junction, which is frequently adopted and finds its justification in the zero-current theorem [21].

In this context  $T$  is given by

$$T = \text{Tr} \{ \Gamma_L G \Gamma_R G^\dagger \} \quad (10)$$

$$\Gamma_\alpha = i[\Sigma_\alpha - \Sigma_\alpha^\dagger] \quad (11)$$

$$\Sigma_\alpha = H_{M\alpha} G_{\alpha\alpha}^0 H_{\alpha M} \quad (12)$$

$$\alpha = \text{L, R}, \quad (13)$$

where the indices L,R refer to the coupling to the left (L) and the right (R) electrode and can be obtained from the self energies of the respective coupling regions as shown in Eq. (11). The self energies in turn are obtained in a partitioning approach as depicted in Eq. (12). Here, the index M refers to the molecule. Eq. (12) requires in principle the exact knowledge of the isolated lead surface Green function  $G_{\alpha\alpha}^0$  for both sides of the junction ( $\alpha = \text{L, R}$ ). In the wide band approximation, which has been adopted throughout this work, the coupling self energies provide an overall widening of the molecular energy levels, in particular at the thiol bridges, due to the interaction with the energy continuum provided by the metal [6]. This approximation introduces a coupling between molecule and electrodes parameterized by a coupling strength  $\delta$  which replaces the evaluation of Eq. (12).

The Green function  $G$  represents the entire system and is to be obtained from a partition approach leading to:

$$G_{MM} = \left[ G_{MM}^0{}^{-1} - \Sigma_L - \Sigma_R \right]^{-1}, \quad (14)$$

where the superscript 0 refers to the Green function of the bare molecule, obtained from the *ab initio* incremental scheme to be discussed below in Sec. 2.2. (The scheme is displayed for the key quantity T, but has been shown in earlier applications to also hold for the self energy  $\Sigma$ , hence for the Green function itself, cf. Ref. [32, 33, 34]).

### 3 Results and Discussion

The theory presented has been applied to both meta- and para-dithiolbenzene. A Valence-double-zeta (vdz) basis set with polarization functions was used throughout the calculations, henceforth denoted as set *A*. For the purpose of test calculations a smaller basis set (vdz without polarization functions) denoted as set *B* was used as well. In a first preparatory step localized HF orbitals were obtained for the molecules employing the Pipek-Mezey option of the program package MOLPRO [38]. The four-index transformation was accomplished by means of the HF program package WANNIER [39] and the subsequent correlation calculations were performed by the program GREENS developed in our laboratory [32, 33]. First the self energy and the Green function were calculated for the bare molecule to various levels of accuracy according to the incremental scheme. The Green function was then inserted into the Landauer formalism in the frame of the wide band approximation to obtain the transmission coefficient  $T$  across a molecular junction with gold electrodes.

#### 3.1 meta-dithiolbenzene

The incremental scheme leaves the partitioning of the molecule into different regions to the user. In the left panel of Fig. 2 the partitioning underlying the following analysis for meta-dithiolbenzene is depicted. The parts denoted I and IV comprise the thiol bridges, while parts II and III constitute the carbon ring. Of course by intuition a partitioning of the carbon ring and its  $\pi$  system would not seem physically reasonable, and indeed this will be confirmed in the end. At this stage, however, we would like to demonstrate the usefulness of a local analytic tool in analyzing precisely such questions. With this partitioning the incremental scheme is applied both to the correction  $\gamma$  to the HOMO-LUMO gap and the transmission coefficient  $T$ .

Throughout this work,  $T$  is evaluated at the Fermi-level which was determined by imposing the charge neutrality condition for the extended system under consideration.

To illustrate the procedure, we first performed calculations on meta-dithiolbenzene using the basis set B. The results are summarized in Tab. 1. The calculations were done for a value of 3 eV for the external coupling parameter  $\delta$ . The molecule was partitioned into four increments numbered I, II, III and IV as indicated in the left panel of Fig. 2. The third row of Tab. 1 shows the results when we consider only all one-body increments denoted as 'S'. The correction for the HOMO-LUMO gap amounts to 2.414 eV if the correlation of the electrons is calculated by means of MP2 (second order Møller-Plesset theory). This result can be improved when next-neighbored two-body increments (denoted as 'nn-D') are considered additionally. By comparing the last two entries in the second column it can be noticed that including only one-body increments and two-body increments in the calculation reproduces almost the correlation contribution of the whole molecule. The same can be noticed when the Epstein-Nesbet theory to second order (EN2) is applied to calculate the correlation contribution. The results are depicted in the third column. Here the values are somewhat increased with respect to the MP2 results, because beside the Fock contributions of the diagonal elements of  $H^R$  the coulomb- and the exchange contributions of the diagonal elements of  $H^R$  are included in EN2 while MP2 only considers the Fock contributions of the diagonal elements of  $H^R$  [31]. The calculated values obtained by applying a full diagonalization for all one-body increments is given in the fourth column. The results show notably the local properties of the correlation contributions, since the one-body increments include the main part of the correlation energies apart from a little difference which mainly is included in the two-body increments. The same observation can be made for the transmission coefficient. The full correlation contribution (in the sense that all increments are accounted for, meaning the entire molecule has been correlated) is approximated by just considering one-body and two-body increments (S and D). So it can be stated that it is unnecessary to include  $n$ -body increments with  $n > 2$ . This fact gives rise to an important conclusion: The numerical effort for the correlation calculation can be lowered drastically. For this purpose the one-body increments are treated by full diagonalization because they include the main part of the correlation while the two-body increments could even be treated by perturbation theory.

In all of the following calculations, however, diagonalization is performed for all increments and the basis set A is employed. Higher ordered increments will again be shown to be of minor significance.

For this case we again start by discussing the results for  $\gamma$  as shown in Tab. 2. Again the row denoted 'S' refers to the result including all one-body increments while 'S+D' also accounts for all two-body increments.

The one-body increments account for most of the correction of the HOMO-LUMO gap, changing the HF value of 11.619 eV by an amount of 5.712 eV. Including all two-body increments brings the HOMO-LUMO gap down by another 1.711 eV. These calculations were done without coupling to the gold electrodes.

Once the coupling is switched on, the Landauer theory allows to calculate the transmission coefficient  $T$ . In Fig. 3  $T$  is calculated in dependence of the coupling  $\delta$ . Varying  $\delta$  might be thought of as modeling different geometries at the junctions continuously, for example the distance between the electrodes and the molecule. In order to establish the connection to more realistic descriptions we have run a test calculation to estimate typical values of the gold-sulfur coupling for a typical covalent Au-S-distance of 2.38 Å [40] with the program package MOLPRO [38] and found coupling integrals in the range of 4 to 5 eV. The HF results are depicted by dashed lines while the solid line includes the correlation effects. The transmission sets on as soon as a finite  $\delta$  is chosen and then increases monotonously with  $\delta$  to a peak value at around 8 eV. With still increasing coupling the transmission then declines again. The interpretation of this behaviour is as follows: As the coupling is switched on, the thiol states will hybridize with the gold atoms, leading to a broadening of the respective molecular states at the gap, pressing electron density into the former HOMO-LUMO gap. Conductance then becomes possible. With ever increasing coupling the broadening of the molecular states then leads to distributing electronic density into the tails of the spectrum away from the gap region, thus lowering the transmission again. The overall tendency is the same for HF and

correlated results. The role of the correlation corrections is to increase the transmission across the junction quantitatively to some extent.

Selected typical values of  $\delta$  are taken to investigate the incremental scheme. Tab. 3 displays the results for the transmission coefficient  $T$ . The denomination of the rows is as above with 'S' referring to one-body increments only and 'S+D' including the two-body corrections as well. Calculations were done for three different values of the external coupling parameter  $\delta$ , corresponding to the increasing branch (4 eV), the peak region (6 eV) and the decreasing branch (10 eV) of the graph in Fig. 3. (As estimated above a typical covalent situation would be expected to be situated between 4 and 5 eV).

In all three cases the HF values are corrected to some extent by the one-body increments. The two-body increments then only give minor corrections being an order of magnitude smaller. For  $\delta = 6$  eV the HF value of 0.576 is corrected by the one-body increments by an amount of 0.048 or 8% to 0.624. The inclusion of two-body increments only contributes another 0.007. This drop establishes the rapid convergence of the incremental scheme.

### 3.2 para-dithiolbenzene

For the sake of comparison and to elucidate the role of the  $\Pi$ -system we also did calculations on the para-dithiolbenzene, which is sketched in the right panel of Fig. 2. Contrary to its meta-version it has an inversion symmetry with respect to its center of mass. Nonetheless we decided to split the carbon ring again into two asymmetric parts, a larger one (region IV, upper part) and a smaller one in the lower part, denoted as part II. We would like to use the incremental scheme to investigate how the different parts contribute to the correlation effects.

The results are shown in Tab. 4 for both the correlation correction  $\gamma$  to the HF HOMO-LUMO gap and the transmission coefficient  $T$ . The terms 'S', 'S+D' and 'S+D+T' refer to inclusion of one-body, two-body and three-body increments. As in the case of the meta system discussed in the previous section, most correlation corrections are assessed with the one-body increments, which correct the HF value of the HOMO-LUMO gap of 11.309 eV by an amount of 6.021 eV. Inclusion of two-body increments leads to an additional correction of 1.041 eV, while the three-body increments together only amount to another -0.003 eV. This confirms that converged results are already obtained on the two-body increment level and justifies the cutoff applied to the incremental series after the two-body contributions for the calculations on the meta-dithiolbenzene in the previous section. It is important to note that the incremental scheme thus allows for a well-monitored and significant simplification in the numerical effort, since the space to be diagonalized for two-body increments is in general significantly smaller than with three regions included. As can be seen from the last column in Tab. 4, these findings are confirmed for the transmission coefficient  $T$  in very much the same way. As for the case of meta-dithiolbenzene, the convergence is even faster than for the gap correction. The HF value is changed from 0.274 by 0.054 or 20% to 0.328 by the one-body increments alone. Two-body increments only correct by -0.006 and three-body increments contribute a meager -0.001.

We now turn to an analysis of the carbon ring contributions. To this end we check explicitly the combinations of the two-body increments where one part of the ring is associated with the left thiol-bridge or where both parts are included and register their influence on the gap correction. The upper and lower part (increments IV and II) are combined with the left thiol-group (region I in the right panel of Fig. 2) to give the combinations '1+4' and '1+2', respectively, in Tab. 4. The improvements on top of the one-body correlation contributions are virtually negligible, amounting to 0.004 eV and zero, respectively. On the other hand, the two-body increment '2+4', which describes the complete carbon ring, gives a large contribution of 0.543 eV. Hence the inclusion of the entire ring system is essential for a quantitative description. This analysis shows that the incremental scheme might not only be used as a method to reduce numerical cost, but could at the same time serve as an analytic tool with a local resolution.

## 4 Conclusions

This work introduces an incremental scheme based on local HF orbitals to construct the self energy and ultimately the Green function with correlations included in an *ab initio* way. The scheme has been carried over from the case of translationally invariant systems to heterogeneous systems such as molecular junctions. The theory combines different ideas into a feasible procedure and has been put forth in detail. The construction of the Green function and related quantities was exemplified by calculations on para- and meta-dithiolbenzene. The correlation correction of the HOMO-LUMO gap was discussed in terms of incremental contributions, and a rapid convergence of the incremental series was found. In the frame of a simple model, the so called wide band approximation, the molecule was then linked to gold electrodes, and the Landauer theory was used to calculate the transmission coefficient across the thus modeled molecular junction. This simple analysis demonstrates how the incremental construction of the Green function could be put to use for the investigation of unconventional systems of high interest. The rapid convergence of the incremental series when applied to the transmission was established. Furthermore the usefulness of the incremental scheme as a local analytic tool became manifest.

In sum the presented approach allows to efficiently assess correlation effects in heterogeneous systems such as molecular junctions and allows to focus on particular parts of the system. We believe the presented technical analysis allows to start with a series of calculations comparing the transmission profile of different molecules in the same environmental context and could thus lead to new insights into the understanding and engineering of molecular junctions.

## 5 Acknowledgements

Valuable discussions with W. H. E. Schwarz (University of Siegen) and M. Dolg (University of Köln) are highly appreciated.

## References

- [1] C. Joachim, J. K. Gimzewski and A. Aviram, *Nature (London)* **408**, 541 (2000).
- [2] M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin and J. M. Tour, *Science* **278**, 252 (1997).
- [3] C. Joachim, J. K. Gimzewski, P. R. Schlittler and C. Chavy, *Phys. Rev. Lett.* **74**, 2102 (1995).
- [4] C. Kergueris, J.-P. Bourgoin, S. Palacin, D. Esteve, C. Urbina, M. Magoga and C. Joachim, *Phys. Rev. B* **59**, 12505 (1999).
- [5] E. G. Emberly and G. Kirczewski, *Phys. Rev. B* **60**, 6028 (1999).
- [6] M. Di Ventra, S. T. Pantelides and N. D. Lang, *App. Phys. Lett.* **76**, 3448 (2000).
- [7] M. Di Ventra, S. T. Pantelides and N. D. Lang, *Phys. Rev. Lett.* **84**, 979 (2000).
- [8] M. P. Samanta, W. Tian, S. Datta *et al.*, *Phys. Rev. B* **53**, R7626 (1996).
- [9] N. D. Lang and Ph. Avouris, *Phys. Rev. Lett.* **84**, 358 (2000).
- [10] G.-L. Ingold and P. Hänggi, *Chem. Phys.* **281**, 199 (2002).
- [11] T. Rakshit, G.-C. Liang, A. W. Ghosh and S. Datta, cond-mat, 0305695 v1, (2003).
- [12] R. Gutiérrez, G. Fagas, K. Richter, F. Grossmann and R. Schmidt, *Europhys. Lett.* **62** (1), pp. 90 (2003); R. Gutiérrez, G. Fagas, G. Cuniberti, F. Grossmann, R. Schmidt and K. Richter, *Phys. Rev. B* **65**, 113410 (2002).
- [13] G. Fagas, A. Kambili and M. Elstner, *submitted to Chem. Phys. Lett.* (2003).
- [14] G. Cuniberti, F. Großmann and R. Gutiérrez, *Advances in Sol. State Phys.*, Vol. **42**, Springer (2002).
- [15] G. Cuniberti, G. Fagas and K. Richter, *Chem. Phys.* **281**, 465 (2002); *Acta Phys. Pol. B.* **32**, 437 (2001).
- [16] J. Heurich, J. C. Cuevas, W. Wenzel and G. Schön, *Phys. Rev. Lett.* **88**, 256803-1 (2002).
- [17] Y. Xue and M. A. Ratner, cond-mat, 0303179 v1, (2003).
- [18] B. Wang, J. Wang and H. Guo, *Phys. Rev. Lett.* **82**, 398 (1998).
- [19] M. H. Hettler, W. Wenzel, M. R. Wegewijs and H. Schoeller, cond-mat, 0207483 v1, (2002).
- [20] A. W. Ghosh and S. Datta, cond-mat, 0303630 v1, (2003).
- [21] T. N. Todorov, G. A. D. Briggs and A. P. Sutton, *J. Phys.: Cond. Mat.* **5**, 2389 (1993).
- [22] M. Paulsson, F. Zahid and S. Datta, cond-mat, 0208183 v1, (2002); to appear in *Nanoscience, Engineering and Technology Handbook*, William Goddard, CRC Press



- [23] M. Petersilka, U. J. Gossmann and E. K. U. Gross, Phys. Rev. Lett. **76**, 1212 (1995).
- [24] T. Grabo, T. Kreibich, S. Kurth and E. K. U. Groß, *Strong Coulomb Correlations in Electronic Structure: Beyond the Local Density Approximation*, edited by V. I. Anisimov (Gordon & Breach) (1998).
- [25] W. M. C. Foulkes, L. Mitas, R. J. Needs and G. Rajagopal, Rev. Mod. Phys. **73**, 33 (2001).
- [26] A. J. Williamson, R. Q. Hood, R. J. Needs and G. Rajagopal, Phys. Rev. B **57**, 12140 (1998).
- [27] L. Mitas, Comput. Phys. Commun. **96**, 107 (1996).
- [28] M. D. Towler, R. Q. Hood and R. J. Needs, Phys. Rev. B **62**, 2330 (2000).
- [29] H. Koch, H. Jørgen, A. Jensen, P. Jørgensen and T. Helgaker, J. Chem. Phys. **93**, 3345 (1990).
- [30] M. Albrecht, P. Fulde, and H. Stoll, Chem. Phys. Lett. **319**, 355 (2000).
- [31] M. Albrecht, P. Reinhardt, and J.-P. Malrieu, Theor. Chem. Acc. **100**, 241 (1998).
- [32] M. Albrecht and J. Igarashi, J. Phys. Soc. Jap. **70**, 1035 (2001).
- [33] M. Albrecht, Theo. Chem. Acc. **107**, 71 (2002).
- [34] M. Albrecht and P. Fulde, Phys. Stat. Sol. b **234**, 313 (2002).
- [35] J. Gräfenstein, H. Stoll, and P. Fulde, Chem. Phys. Lett. **215**, 610 (1993).
- [36] J. Gräfenstein, H. Stoll, and P. Fulde, Phys. Rev. B **55**, 13588 (1997).
- [37] S. Datta, *Electronic Transport in Mesoscopic Systems*, Cambridge University Press, Cambridge (1995).
- [38] MOLPRO, a package of *ab initio* programs designed by H.-J. Werner and P. J. Knowles, version 2002.1, R. D. Amos, A. Bernhardsson, A. Berning, P. Celani, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, P. J. Knowles, T. Korona, R. Lindh, A. W. Lloyd, S. J. McNicholas, F. R. Manby, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, R.M. Pitzer, G. Rauhut, M. Schütz, U. Schumann, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, and H.-J. Werner.
- [39] A. Shukla, M. Dolg, H. Stoll, and P. Fulde, Chem. Phys. Lett. **262**, 213 (1996).
- [40] C. Majumder, T. M. Briere, H. Mizuseki, and Y. Kawazoe, J. Chem. Phys. **117**, 2819 (2002).

**Table 1** Correlation correction  $\gamma$  of the HF-HOMO-LUMO gap of meta-dithiolbenzene (Column 2–4. The values are given in eV).  $\gamma_{\text{diag}}$  labels the correlation correction obtained by full diagonalization. The last column contains  $T$  at the Fermi-level. Coupling to the electrodes is accounted for by applying  $\delta$  with a value of 3 eV.

increments:	$\gamma_{\text{MP2}}$	$\gamma_{\text{EN2}}$	$\gamma_{\text{diag}}$	$T_{\text{MP2}}$
HF (HOMO-LUMO gap: 12.019 eV)				0.108
all S	2.414	2.789	3.900	0.176
all S + nn-D	2.773	—	—	—
all S + D	2.919	3.436	—	0.179
full correlation contribution	2.921	3.439	4.636	0.179

**Table 2** Incremental scheme for the correlation correction  $\gamma$  to the HOMO-LUMO gap. with different coupling constants  $\delta$  (in eV). Row 'S' gives the correlated results with all one-body increments included, row 'S+D' also takes into account all two-body increments.

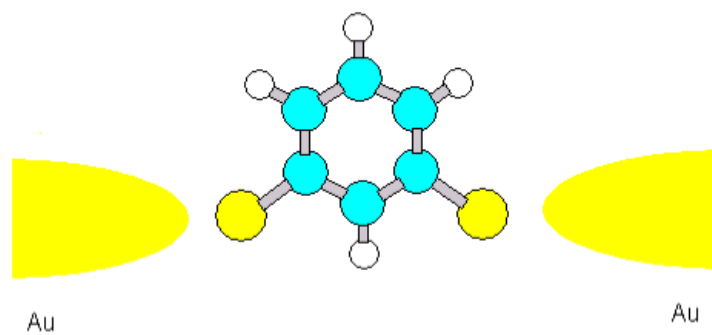
increment	narrowing of the gap	$\Delta$
HF	HF-gap= 11.619	
S	5.712	5.712
S+D	7.423	1.711

**Table 3** Incremental scheme for the transmission coefficient  $T$  at the Fermi-level with different coupling constants  $\delta$ . Row 'S' gives the correlated results with all one-body increments included, row 'S+D' also takes into account all two-body increments.

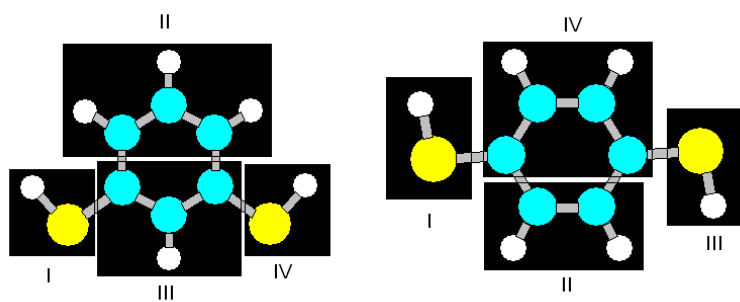
	$\delta = 4.0$	$\delta = 6.0$	$\delta = 10.0$
HF	0.474	0.576	0.603
S	0.526	0.624	0.635
S+D	0.534	0.631	0.640

**Table 4** Incremental scheme for the transmission coefficient  $T$  at the Fermi-level and for the correlation correction  $\gamma$  to the HOMO-LUMO gap (in eV) calculated at a coupling constants  $\delta = 2\text{eV}$ . Row 'S' gives the correlated results with all one-body increments included, row 'S+D' also takes into account all two-body increments while 'S+D+T' states the results up to three-body increments.  $\Delta$  and  $\Delta_T$  monitor the incremental improvement.

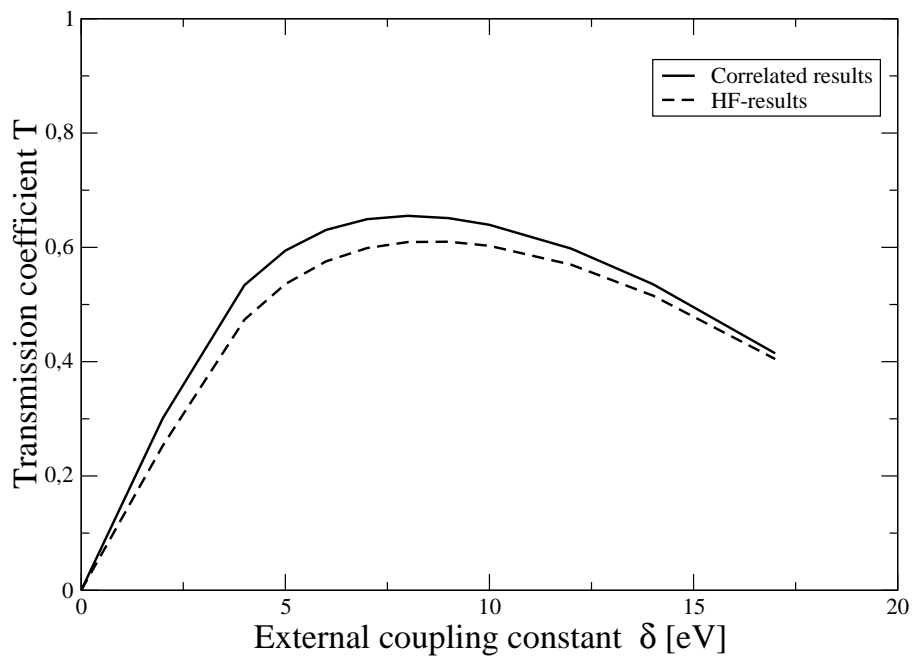
increment	narrowing of the gap	$\Delta$	T	$\Delta_T$
HF	gap=11.309		0.274	
all singles	6.021	6.021	0.328	0.054
1+2	6.021	0.000		
1+4	6.024	0.004		
2+4	6.564	0.543		
all doubles	7.062	1.041	0.322	-0.006
all triples	7.059	-0.003	0.321	-0.001



**Fig. 1** Sketch of meta-dithiolbenzene illustrating the principle arrangement of so-called molecular junctions.



**Fig. 2** Sketch of the incremental scheme, exemplifying a possible partitioning of the meta-dithiolbenzene (left panel) and para-dithiolbenzene (right panel) comprising four parts denoted as I, II, III and IV.



**Fig. 3** Transmission coefficient  $T$  at the Fermi-level for the meta-dithiolbenzene in dependence of the contact parameter  $\delta$  for the HF-results (dashed) as well as for the correlated results with one-body- and two-body increments included (solid).