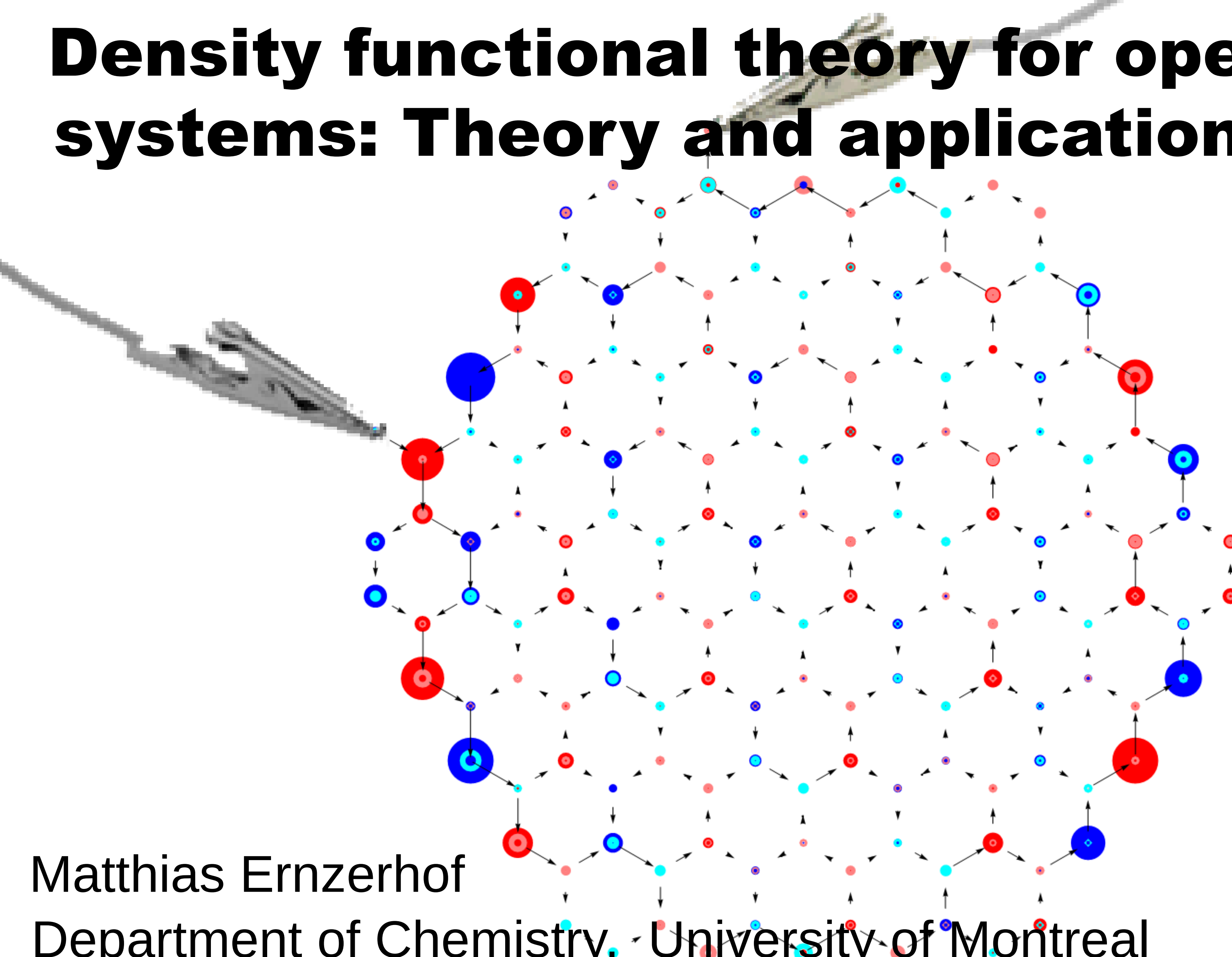
Density functional theory for open systems: Theory and applications



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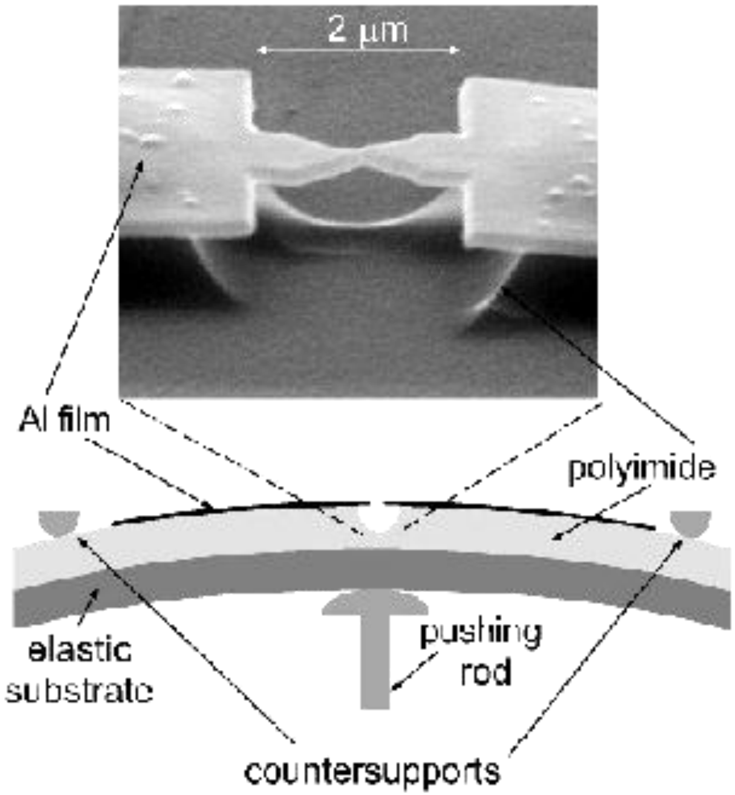
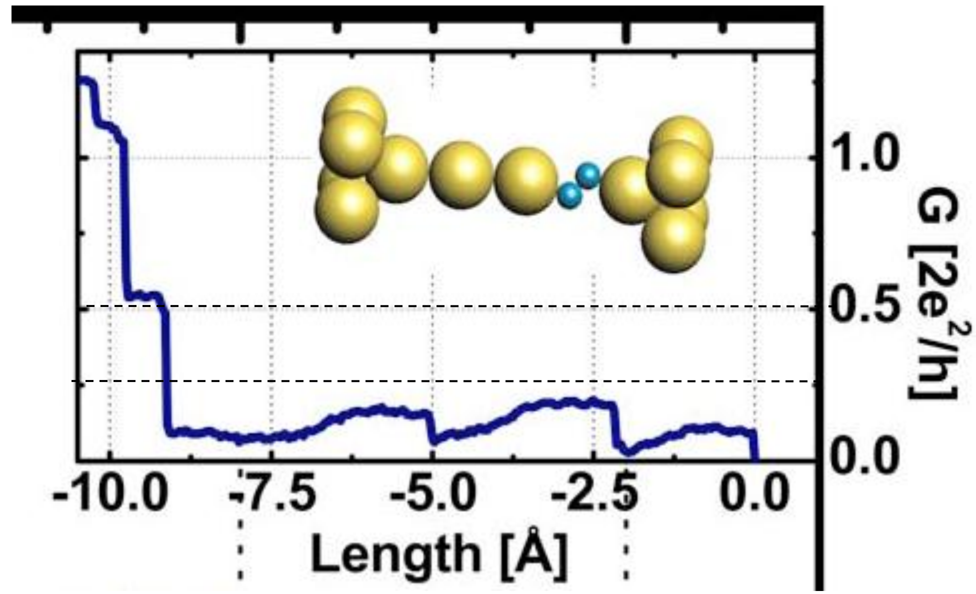
-*Yongxi Zhou*
-*Francois Goyer*
-*Min Zhuang*

Funding and other support: NSERC, CFI, Gaussian.

Molecular electronics





Csonka, Halbritter, Mihály PRB 73, 075405 (2006)

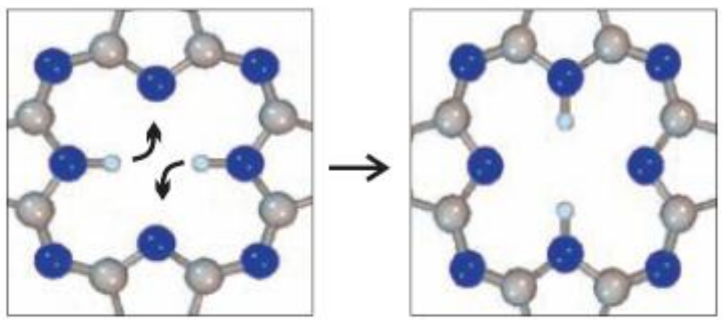
Break junction technique

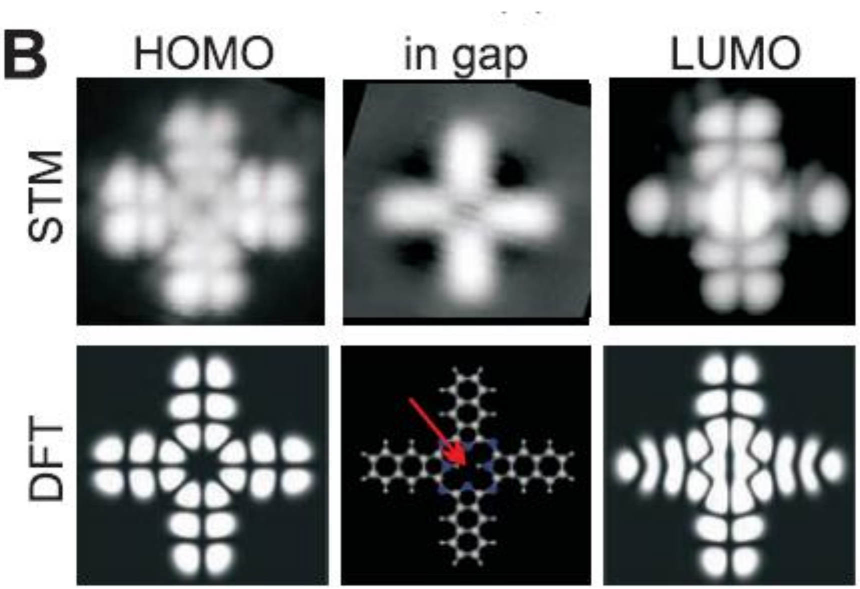
Reed, Zhou, Muller et al., Science 278, 252 (1997); Reichert, Ochs, Beckman et al., PRL, 88, 176804 (2002)

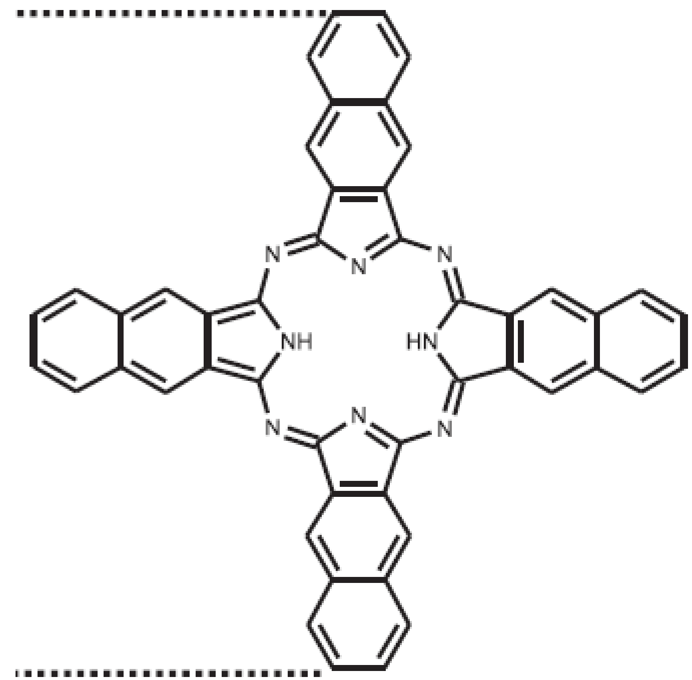
Current-Induced Hydrogen Tautomerization and Conductance Switching of Naphthalocyanine Molecules

Peter Liljeroth,[1*] Jascha Repp,[1,2] Gerhard Meyer[1]

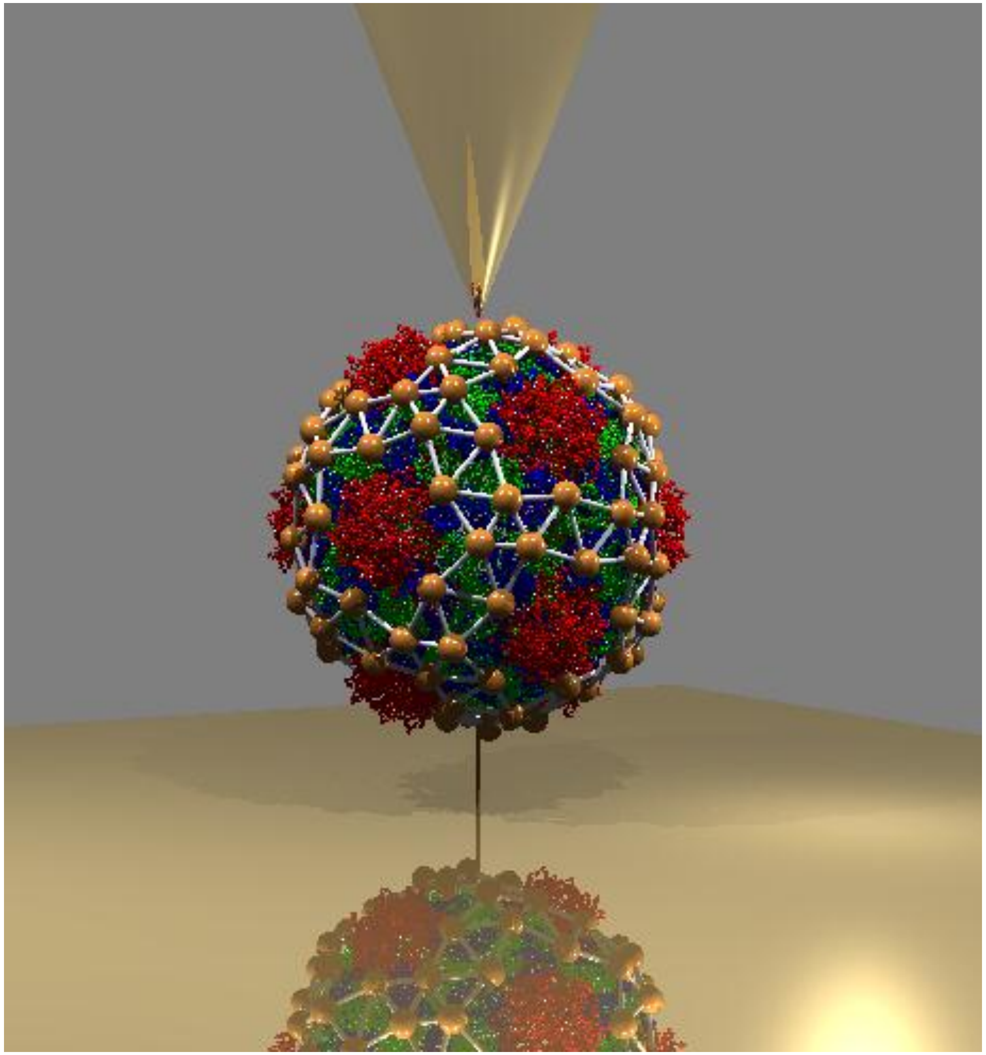
Science 317, 1203 (2007)







Molecular network on a nano particle (A. Blum McGill University)



Resonances in electron scattering by molecules on surfaces

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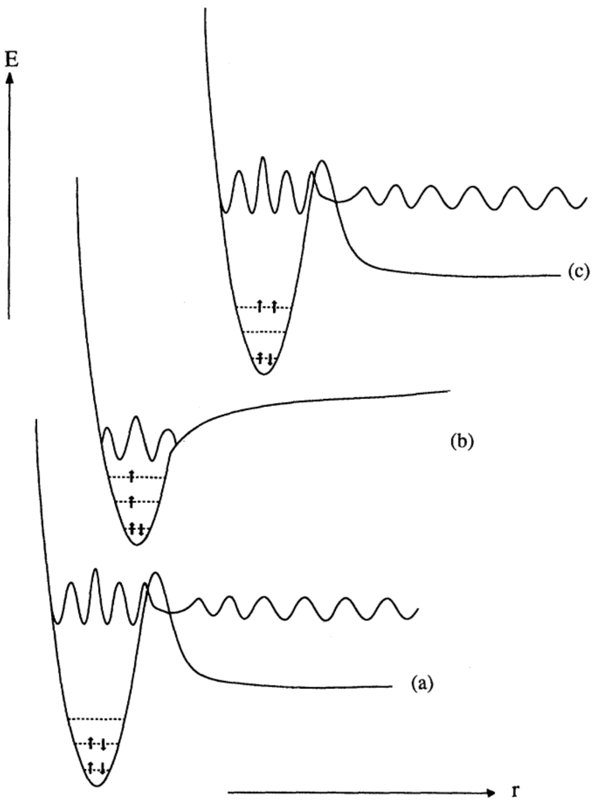
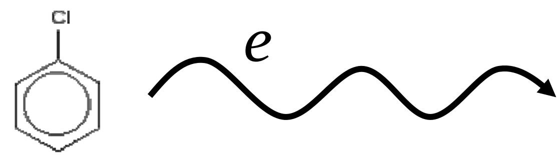
P. J. Rous

Department of Physics, University of Maryland Baltimore County, Catonsville, Maryland 21228

Reviews of Modern Physics, Vol. 64, No. 2, April 1992





$$E = E_0 - i\frac{\Gamma}{2}$$

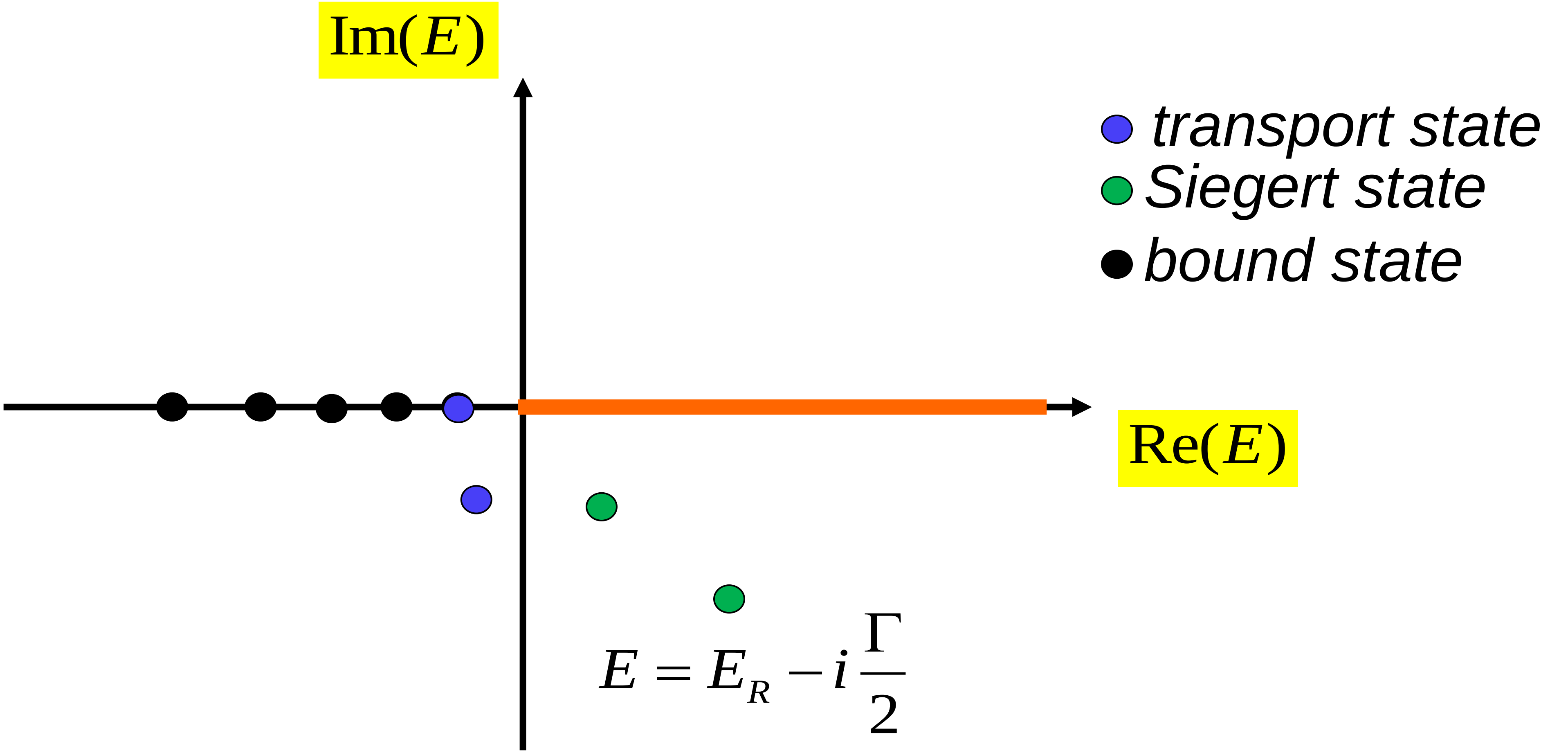
TABLE V. Energies and widths of resonances in elastic electron scattering from chlorobenzene. Theoretical values obtained in this work by CAP/SE (static exchange) and CAP/$\Sigma^{(2)}$ are compared with experimental values. We rely on the values of Burrow *et al.* (Ref. 59) because their spectra are well resolved and show both the $^2\Pi$ and $^2\Sigma$ resonances. Note the error of about 5% for the energy and about 25% for the width estimated for the values of CAP/$\Sigma^{(2)}$ due to the incomplete basis set.

	Energy (eV)			Width (eV)	
Symmetry	Experiment	CAP/SE	CAP/$\Sigma^{(2)}$	CAP/SE	CAP/$\Sigma^{(2)}$
A_1	2.42	5.41	2.92	1.84	1.01
B_1	0.75	2.83	1.27	0.52	0.17
A_2	0.75	2.73	1.29	0.45	0.05

R. Santra and L. S. Cederbaum, J. Chem. Phys. **117**, 5511 (2002).
S. Feuerbacher, T. Sommerfeld, R. Santra, and L. S. Cederbaum, J. Chem. Phys. **118**, 6188 (2003).

Stationary states and boundary conditions

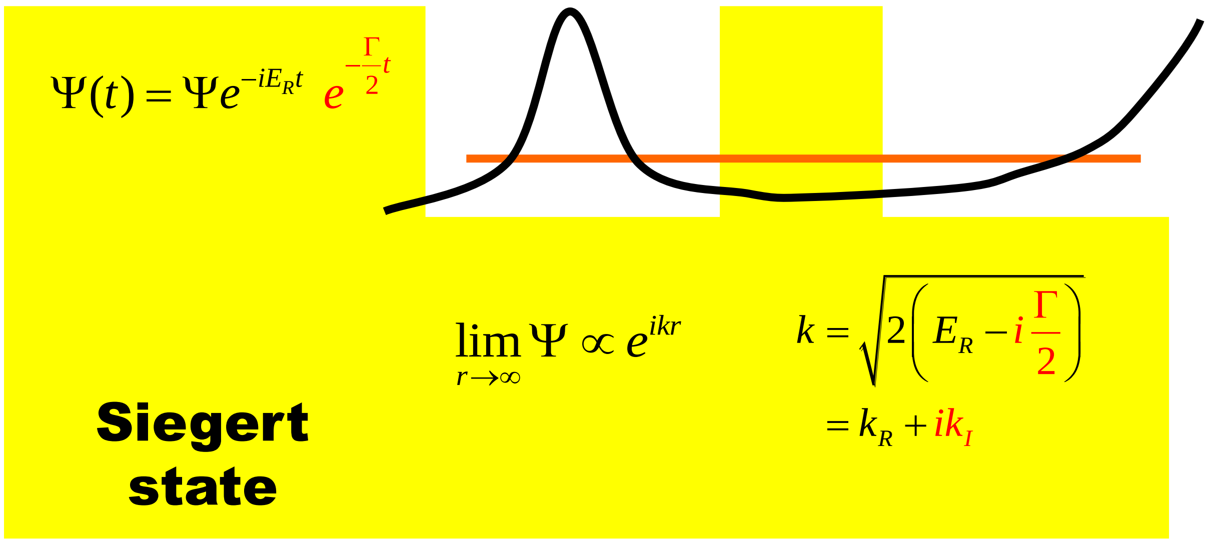
$$H\Psi = E\Psi \qquad H = \sum_{i}^{N}\left(-\frac{1}{2}\Delta_i + v(\vec{r}_i)\right) + \tfrac{1}{2}\sum_{i\neq j}^{N}\frac{1}{\left|\vec{r}_i - \vec{r}_j\right|}$$



$$E = E_R - i\frac{\Gamma}{2}$$

Siegert, Phys. Rev. 56, 750 (1939)

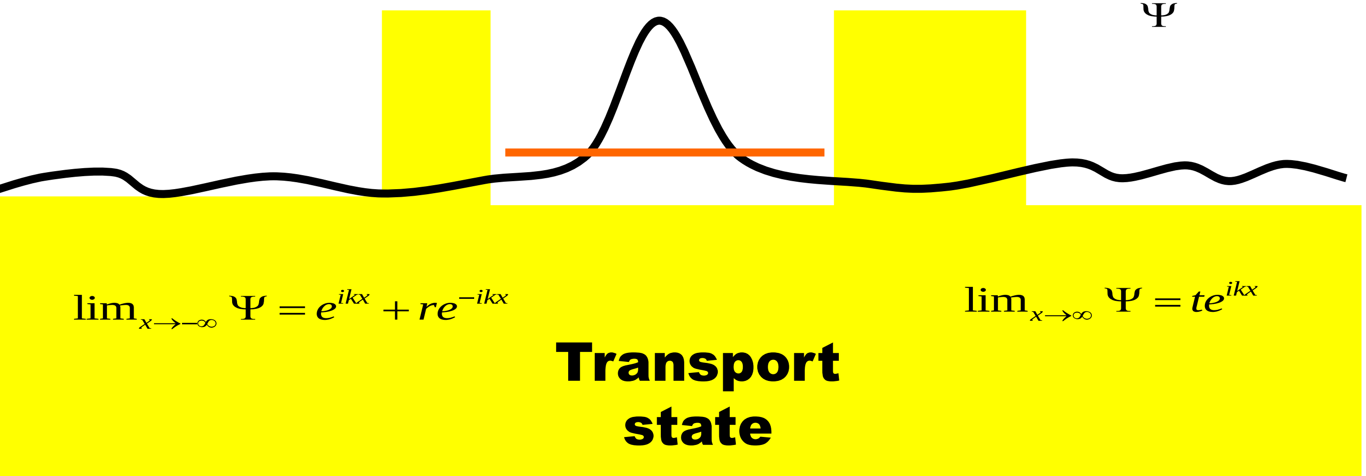
Open systems



$$\langle \Psi | H | \Psi \rangle \neq \langle H\Psi | \Psi \rangle$$

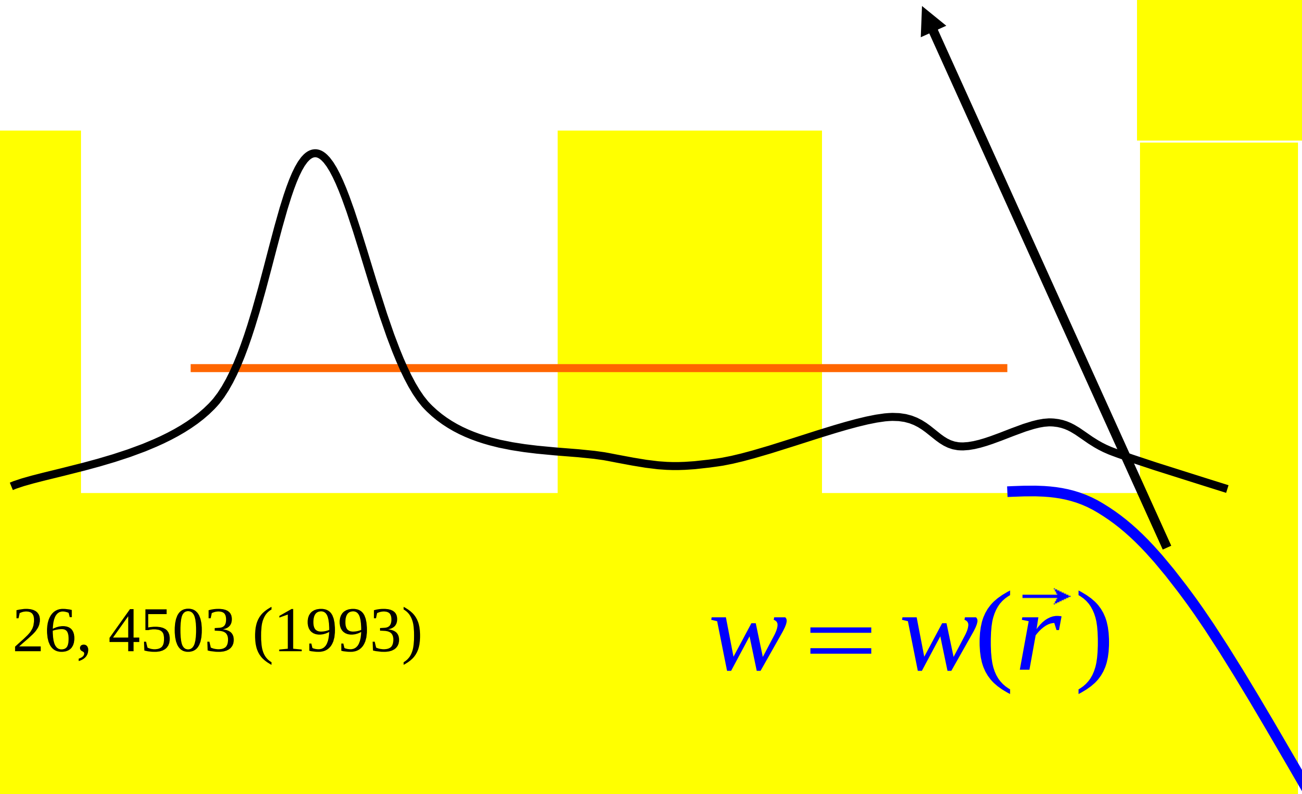
$$E = E^* \Rightarrow I_{in} = I_{out}$$

$$\frac{H\Psi}{\Psi} = E$$



Complex absorbing potentials

$$H \rightarrow H - i\eta w$$



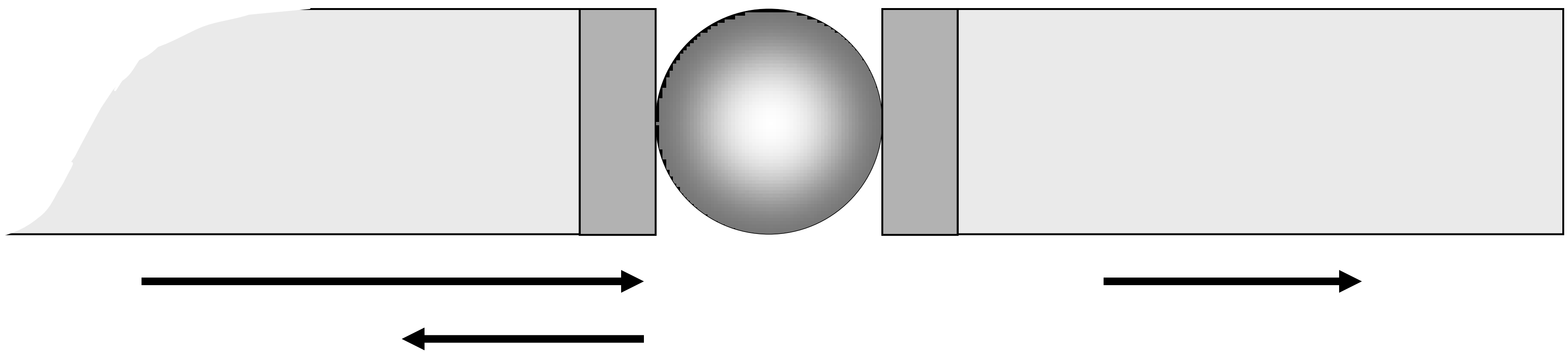
$$w = w(\vec{r})$$

Riss, Meyer, J. Phys. B 26, 4503 (1993)

Muga et al., Phys. Rep. 395 (2004)
Santra, Cederbaum, Phys. Rep. 368 (2002)
Moiseyev, Phys. Rep. 302 (1998)

$$H \,|\, \Psi_i \rangle \; = \; E_i \,|\, \Psi_i \rangle$$

The source-sink potential approach to represent the boundary conditions



$$\Psi_L = \varphi^+ + r\ \varphi^-$$

$$\Psi_R = t\ \varphi^+$$

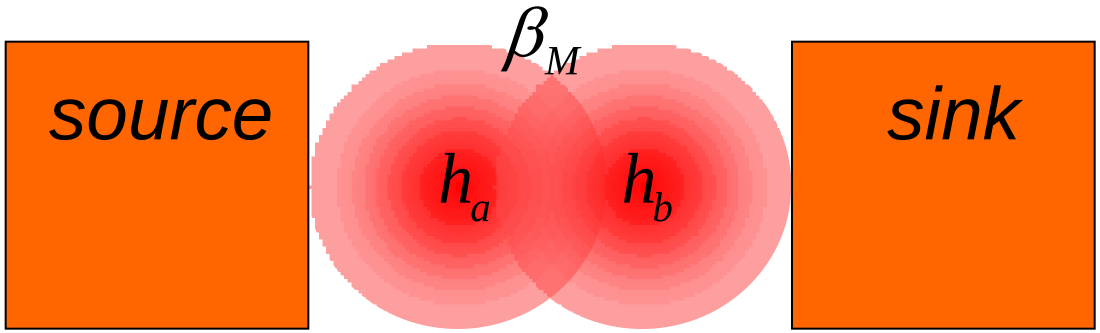
$$\phi_L = \left(\varphi^+ + r\varphi^-\right) f$$

$$\left(-\frac{1}{2}\Delta + v + \Sigma\right)\phi_L = \varepsilon\phi_L$$

$$\frac{\Delta\phi_L}{2\phi_L} - v + \varepsilon = \Sigma(r,\varepsilon)$$

Goyer, Ernzerhof, Zhuang, JCP, 126,144104 (2007)

The source-sink potential approach in tight binding



$$H^{\text{eff}}(r) = \begin{pmatrix} h_a - \sigma_L & \beta_M \\ \beta_M & h_b - \sigma_R \end{pmatrix}$$

$$\sigma_L = i\beta_{LM}\frac{1+r}{1-r}$$

$$\sigma_R = -\beta_{RM}\, i$$

Source and sink potential

Ernzerhof, JCP 126,144104 (2007)

Continuity equation

Ernzerhof, JCP, 125 124104 (2006)

$$H = H_0 - i\eta w \qquad E = E_0 - i\frac{\Gamma}{2} \qquad \Psi(t) = \Psi e^{-iE_R t} e^{-(\Gamma/2)t}$$

$$\frac{d\rho(r,t)}{dt} = -\nabla\vec{j}(r,t) - 2\eta w(r)\rho(r,t)$$

$$\Gamma\rho(r) = \nabla\vec{j}(r) + 2\eta w(r)\rho(r)$$

$$\Gamma\rho(r) = \nabla\vec{j}(r) \qquad -\nabla\vec{j}(r) = +(2\eta w(r) - \Gamma)\rho(r)$$

interior *boundary*

$$N\Gamma = I = 2\eta\langle\Psi|w|\Psi\rangle$$

Complex symmetric Hamiltonians

$$H\,|\Psi_i\rangle = E_i\,|\Psi_i\rangle \qquad \langle\Theta_i|\,H = E_i\langle\Theta_i|$$

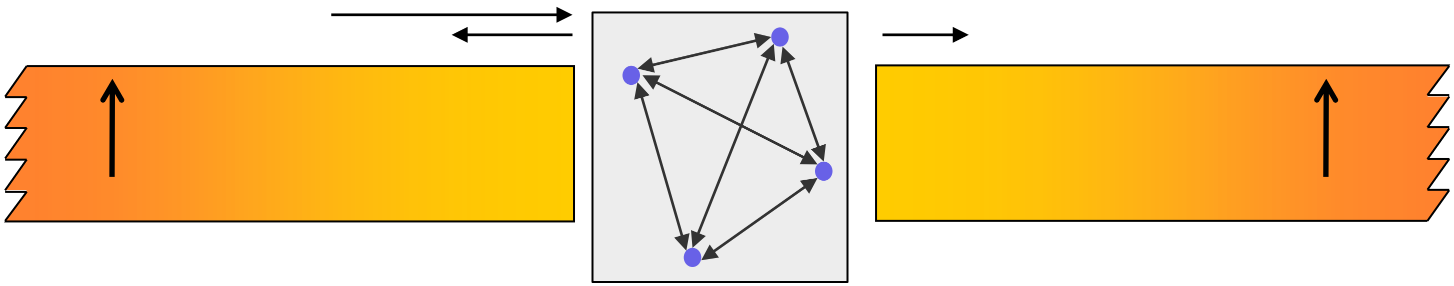
$$\langle\Theta_i\,|\,\Psi_j\rangle = \delta_{ij} \qquad \Theta_i = \Psi_i^{\,*}$$

$$E[\Psi] = \frac{\langle\Psi^*\,|\,H_0 - i\eta w\,|\,\Psi\rangle}{\langle\Psi^*\,|\,\Psi\rangle}$$

$$w = w(\vec{r})$$

$$E_i = \underset{\Psi}{stat}\ E[\Psi]$$

Interacting model



$$H = H_0 + \Sigma_L(r, \varepsilon_F) + \Sigma_R(\varepsilon_F)$$

$$H(r, \varepsilon_F)\Psi = E\Psi \qquad \det(H(r, \varepsilon_F) - E) = 0$$

$$E = \varepsilon_F + E_{Ion}$$

Goker, Goyer, Ernzerhof, JCP, 129 194901 (2008);
Goyer, Ernzerhof, JCP, submitted.

Complex-density functional theory

$$\nu(\vec{r}) = v(\vec{r}) - i\eta w(\vec{r})$$

$$E = E_0 - i\frac{\Gamma}{2}$$

$$\rho(\vec{r}) = \frac{\delta E}{\delta \nu(\vec{r})}$$

(Stationarity principle)

$$\rho(\vec{r}) = \rho_R(\vec{r}) + i\rho_I(\vec{r})$$

A change in the external local potential $\delta v(\vec{r})$

results in a change of the lifetime

Locally defined density functionals

i) $$\rho(\vec{r}) = \frac{\delta E}{\delta v(\vec{r})}$$

Ernzerhof,
PRA 50, 4593 (1994)

ii) $$F[\rho] = E[v] - \int d^3r\, \rho(\vec{r})v(\vec{r})$$

iii) $$\begin{aligned} F[\rho_0 + \Delta\rho] &= F[\rho_0] - \int d^3r\, v_0(\vec{r})\Delta\rho(\vec{r}) \\ &+ \frac{1}{2!}\int d^3r d^3r'\, \xi^{(1)}{}_{\rho_0}(\vec{r},\vec{r}')\Delta\rho(\vec{r})\Delta\rho(\vec{r}') \\ &+ \frac{1}{3!}\int d^3r d^3r' d^3r''\, \xi^{(2)}{}_{\rho_0}(\vec{r},\vec{r}',\vec{r}'') \\ &\times \Delta\rho(\vec{r})\Delta\rho(\vec{r}')\Delta\rho(\vec{r}'') \\ &+ \ldots \end{aligned}$$

iv) $$\xi^{(1)}{}_{\rho_0}(\vec{r},\vec{r}') = -\left(\chi^{(1)}{}_{v_0}(\vec{r},\vec{r}')\right)^{-1}$$

$$\chi^{(1)}{}_{v_0}(\vec{r},\vec{r}') = \frac{\delta^2 E}{\delta v(\vec{r})\delta v(\vec{r}')}$$

Potential response functions

$$\rho = \frac{\delta E}{\delta v}$$

$$\xi^{(1)}{}_{\rho_0}(\vec{r},\vec{r}\,') = -\left(\chi^{(1)}{}_{v_0}(\vec{r},\vec{r}\,')\right)^{-1}$$

$$\begin{aligned} \xi^{(2)}{}_{\rho_0}(\vec{r},\vec{r}\,',\vec{r}\,'') \quad &= \quad -\int d^3r_1 d^3r_2 d^3r_3 \\ \times \quad & \xi^{(1)}{}_{\rho_0}(\vec{r},\vec{r}_1)\xi^{(1)}{}_{\rho_0}(\vec{r}\,',\vec{r}_2)\xi^{(1)}{}_{\rho_0}(\vec{r}\,'',\vec{r}_3) \\ \times \quad & \chi^{(2)}{}_{v_0}(\vec{r}_1,\vec{r}_2,\vec{r}_3) \end{aligned}$$

Constraint search approach

$$\mathrm{H} = T + v + V_{ee}$$

$$v(\vec{r}) = v(\vec{r}) - i\eta w(\vec{r})$$

$$E_i = \underset{\Psi}{stat}\left(\int d^3r\, v(\mathbf{r})\rho(\mathbf{r}) + \frac{\left\langle \Psi^* \mid T + V_{ee} \mid \Psi \right\rangle}{\left\langle \Psi^* \mid \Psi \right\rangle} \right)$$

$$\rho(\vec{r}) = \frac{\left\langle \Psi^* \mid \hat{\rho}(\vec{r}) \mid \Psi \right\rangle}{\left\langle \Psi^* \mid \Psi \right\rangle}$$

$$F[\rho, N] = \min_{\mathrm{Re}(E)} \underset{\Psi -> \rho, N}{\mathrm{stat}} \frac{\left\langle \Psi^* \mid T + V_{ee} \mid \Psi \right\rangle}{\left\langle \Psi^* \mid \Psi \right\rangle}$$

$$E = \underset{\rho}{stat}\left(\int d^3r\, \rho(\vec{r}) v(\vec{r}) + F[\rho, N] \right)$$

Kohn-Sham-type equation

$$h_s = -\frac{1}{2}\Delta + v_s(\vec{r})$$

$$h_s \varphi_i = \varepsilon_i \varphi_i$$

$$\rho(\vec{r}) = \sum_i^N \varphi_i(\vec{r}) \varphi_i(\vec{r})$$

$$T_s[\rho] = \sum_i^N \langle \varphi_i^* | T | \varphi_i \rangle$$

$$E = T_{s,}[\rho] + \int d^3 r\, v(\vec{r})\rho(\vec{r}) + \frac{1}{2}\int d^3 r d^3 r' \frac{\rho(\vec{r})\rho(\vec{r})}{|\vec{r} - \vec{r}'|} + E_{xc}[\rho]$$

$$v_s(\vec{r}) = v(\vec{r}) - i\eta w(\vec{r}) + \int d^3 r' \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} + v_{XC}(\vec{r})$$

$$v_{xc} = \frac{\delta E_{xc}[\rho]}{\delta \rho}$$

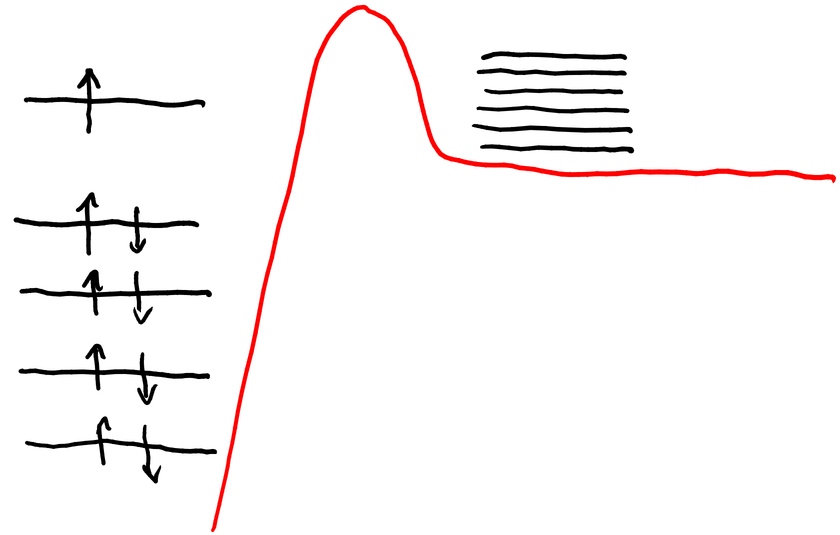
Functionals of the complex density

$$E_x^{LDA} = C_x \int d^3 r \, \rho^{4/3}(\vec{r})$$

$$= C_x \int d^3 r \, |\rho(\vec{r})|^{4/3} \, e^{i\frac{4}{3}\overbrace{\left(\varphi(\vec{r}) + n2\pi\right)}^{\phi}}$$

$$\phi \in (-\pi, \pi)$$

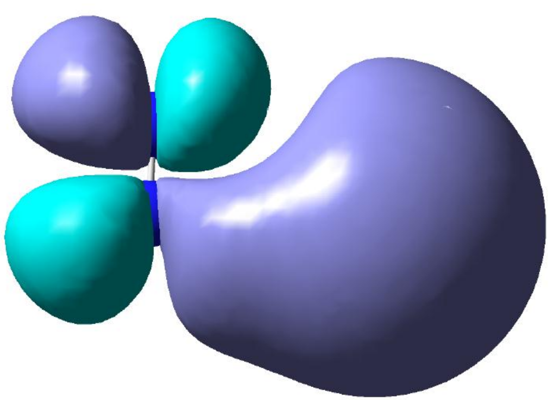
Metastable system



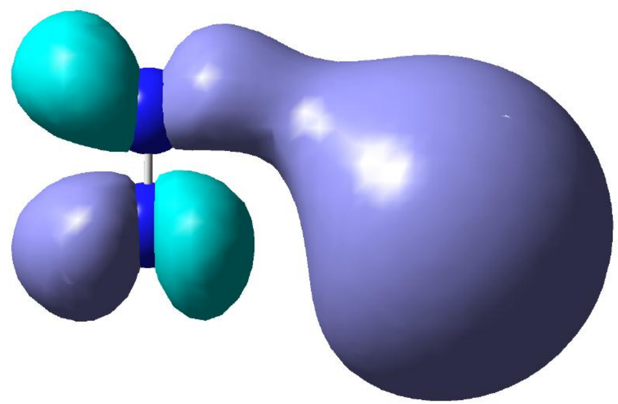
		Anion		*Neutral*	
		E_{Re}	E_{Im}	E_{Re}	E_{Im}
HF	η=0.01	-108.92439	-0.74682E-2	-108.86047	-0.80089E-4
	η=0.03	-108.91512	-0.22156E-1	-108.86043	-0.23173E-3
$KS(E_x)$	η=0.01	-107.67666	-0.56397E-2	-107.63396	-0.13564E-3
	η=0.03	-107.67184	-0.14751E-1	-107.63389	-0.36425E-3
$KS(E_{xc})$	η=0.01	-108.67181	-0.56980E-2	-108.58001	-0.13701E-3
	η=0.03	-108.66694	-0.14909E-1	-108.57995	-0.31955E-3

Highest occupied molecular orbital of KS(E_x)

Re



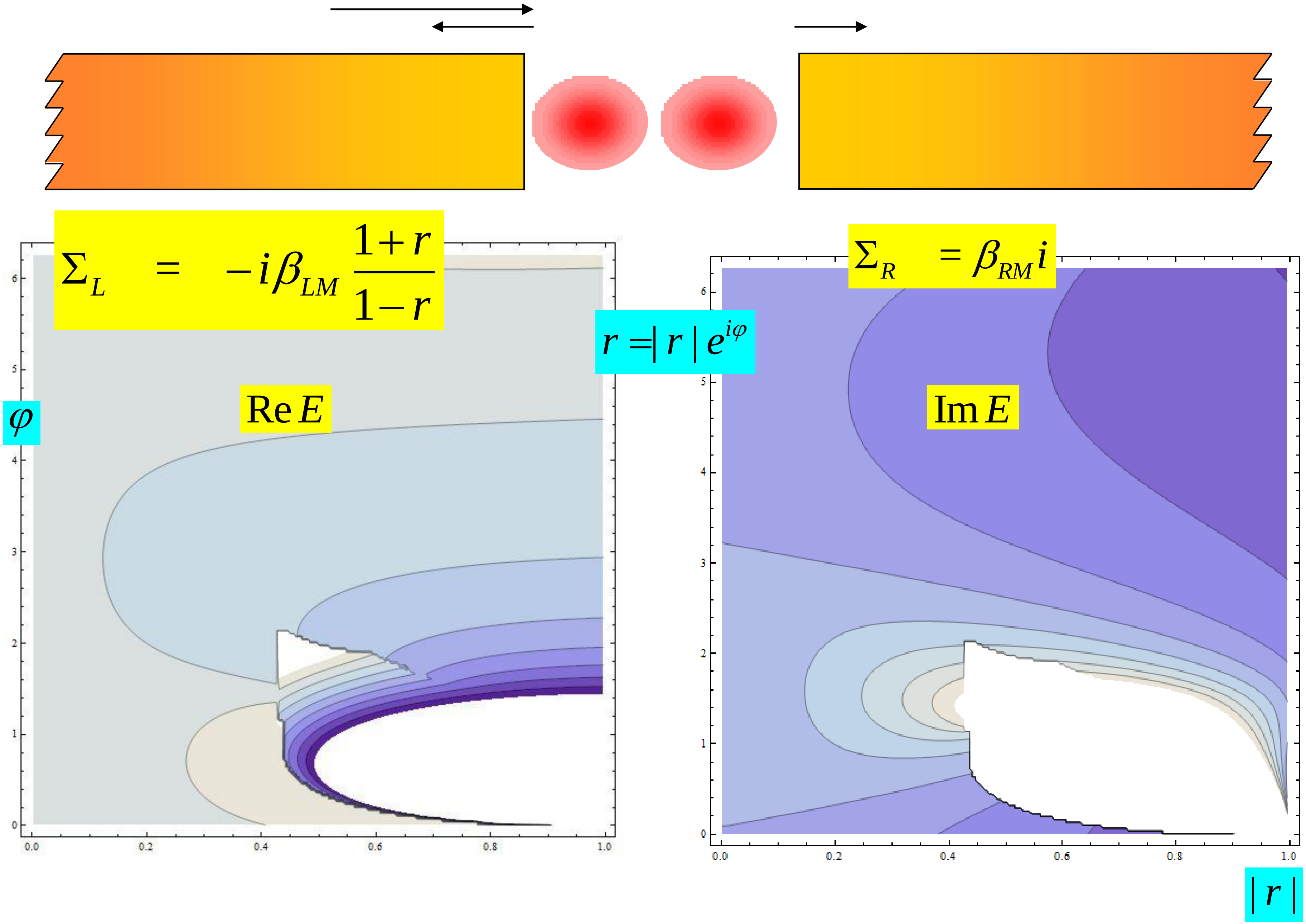
Im *x100*



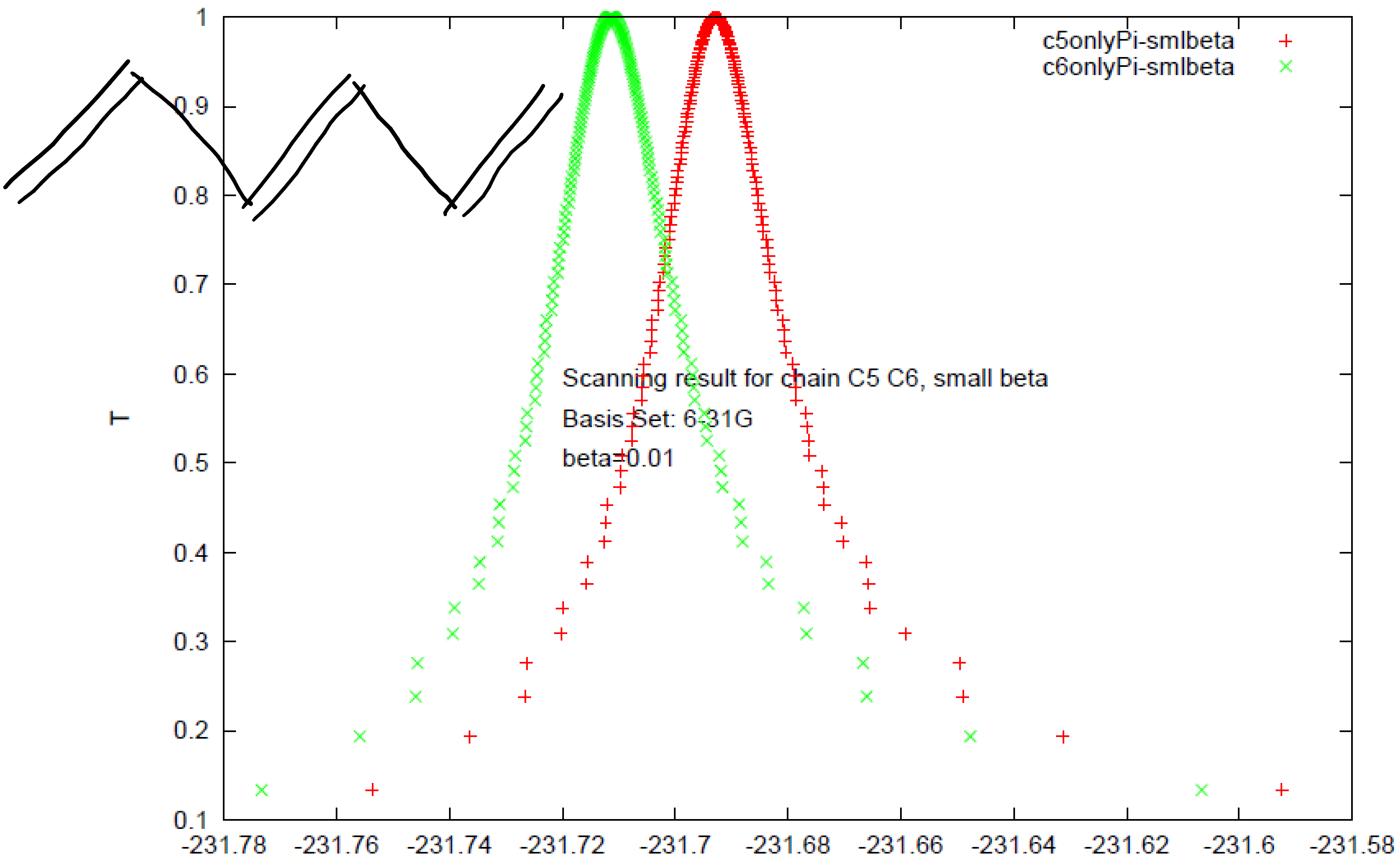
Exchange-correlation contributions

		Exchange		*Correlation*	
		E_{Re}	E_{Im}	E_{Re}	E_{Im}
HF	η=0.01	-13.30248	0.00980	0	0
	η=0.03	-13.30393	0.02825	0	0
$KS(E_x)$	η=0.01	-12.08469	0.00742	0	0
	η=0.03	-12.08621	0.02115	0	0
$KS(E_{xc})$	η=0.01	-12.08469	0.00742	-0.98084	0.00112
	η=0.03	-12.08621	0.02115	-0.98129	0.00311

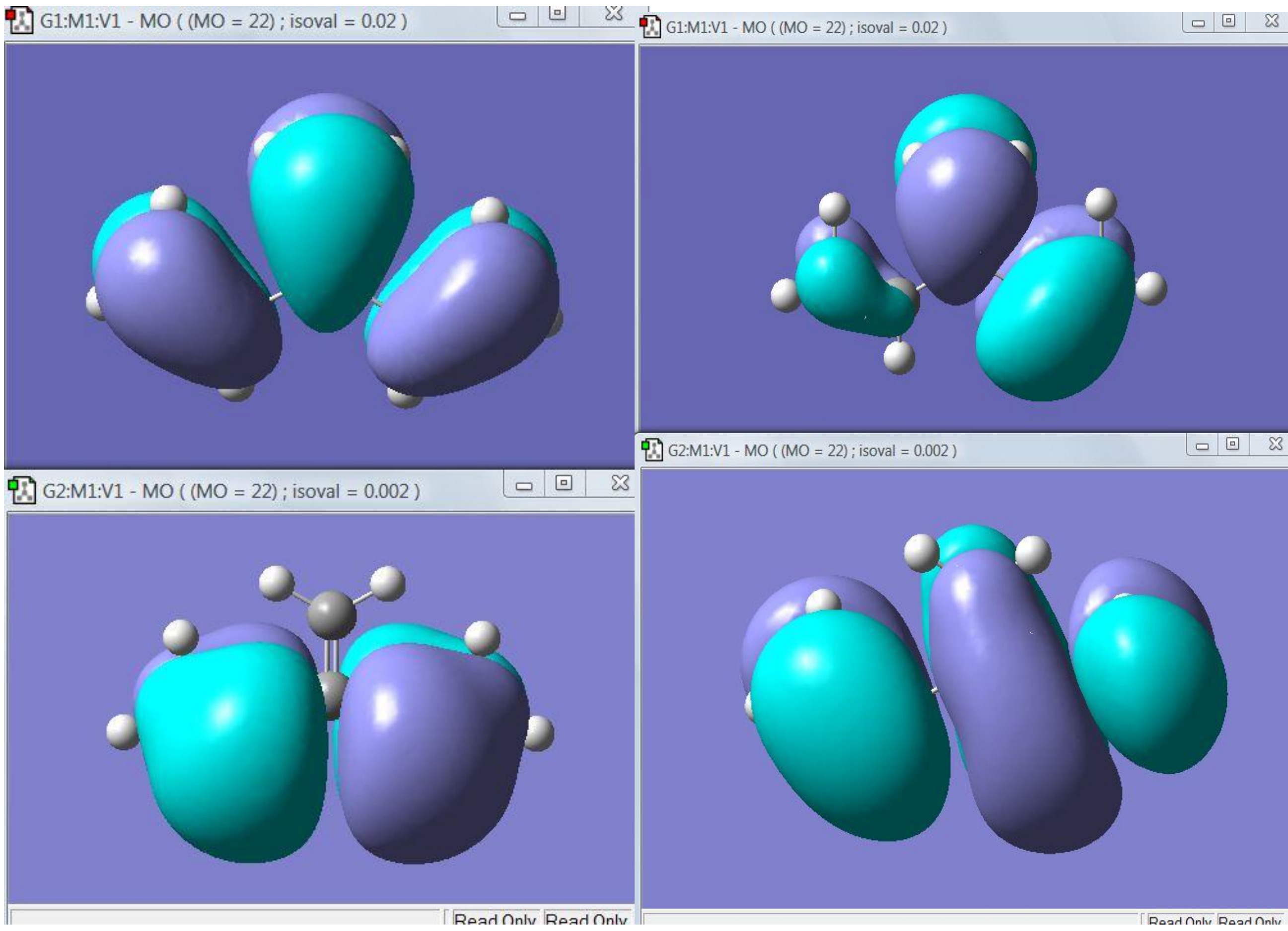
Hartree-Fock self-consistent calculation: Diatomic gold wire



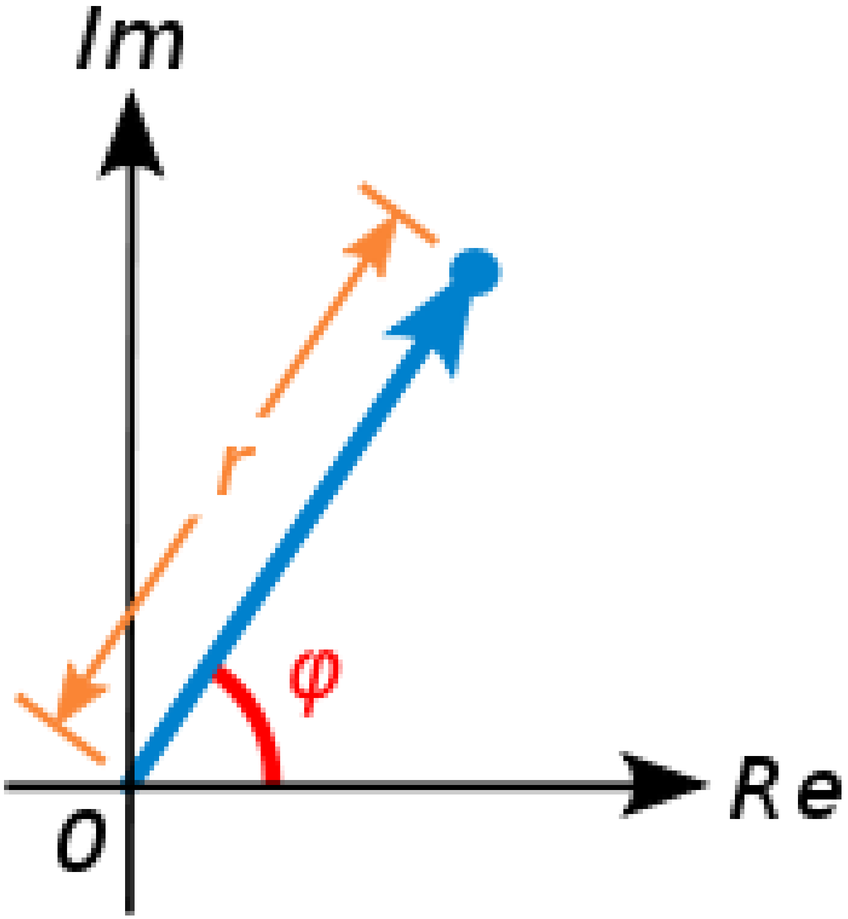
KS(E_x) transport calculations with source and sink potentials



HOMOs for T(E)=1 and T(E)≈0



Electron interaction in the complex plane



$$\langle \Psi | H | \Psi \rangle \neq \langle H\Psi | \Psi \rangle$$

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Complex Extension of Quantum Mechanics

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(Received 12 August 2002; published 16 December 2002)

Requiring that a Hamiltonian be Hermitian is overly restrictive. A consistent physical theory of quantum mechanics can be built on a complex Hamiltonian that is not Hermitian but satisfies the less restrictive and more physical condition of space-time reflection symmetry ($\mathcal{PT}$ symmetry). One might expect a non-Hermitian Hamiltonian to lead to a violation of unitarity. However, if $\mathcal{PT}$ symmetry is not spontaneously broken, it is possible to construct a previously unnoticed symmetry $\mathcal{C}$ of the Hamiltonian. Using $\mathcal{C}$, an inner product whose associated norm is positive definite can be constructed. The procedure is general and works for any $\mathcal{PT}$-symmetric Hamiltonian. Observables exhibit $\mathcal{CPT}$ symmetry, and the dynamics is governed by unitary time evolution. This work is not in conflict with conventional quantum mechanics but is rather a complex generalization of it.