Effective momentum – momentum coupling in a correlated electronic system: the diamagnetism of benzene.

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Based on the PhD thesis of T. V. Trevisan; UNICAMP-2019

Outline:

i) Generalities

ii) Motivation: Diamagnetism of benzene

iii) Model systems: the Hubbard rings

iv) Application to the diamagnetism of benzene

v) Beyond the Born – Oppenheimer approximation and a new effective interelectronic interaction

vi) Conclusions and comments

Generalities

i) In Nature, strongly interacting many – body systems is the general rule rather than an exception. Possible separation of time, length and energy scales simplifies the dynamics. Useful example; *electronic systems*.

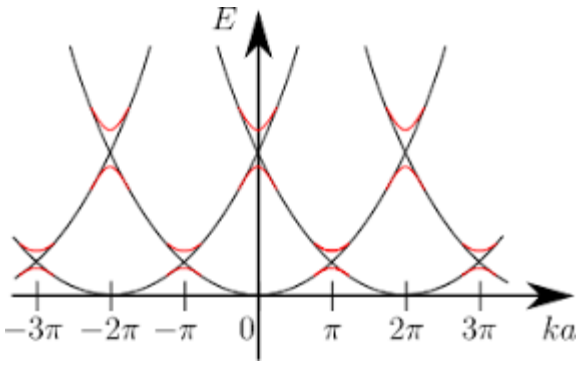
ii) Low energy physics of many – electron systems; Coulomb interaction is all there is! Relativistic corrections: spin – orbit, spin – spin (magnetic dipole), and orbit – orbit (Breit – Darwin) interactions are all of electromagnetic origin.

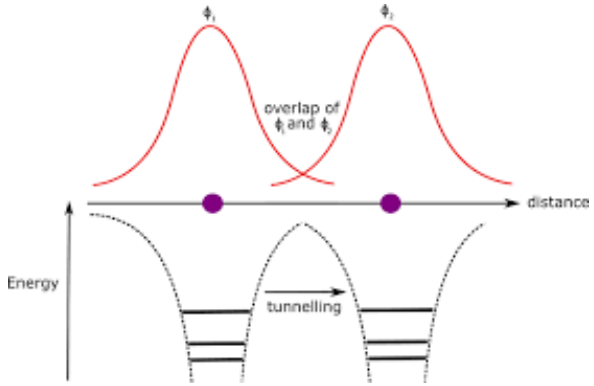
iii) No secret about the basic interaction underlying a many – electron system! Powerful computers ⟹ ingenious numerical and simulation methods, but…

iv) More insight is gained if they are implemented in simpler *effective models*.

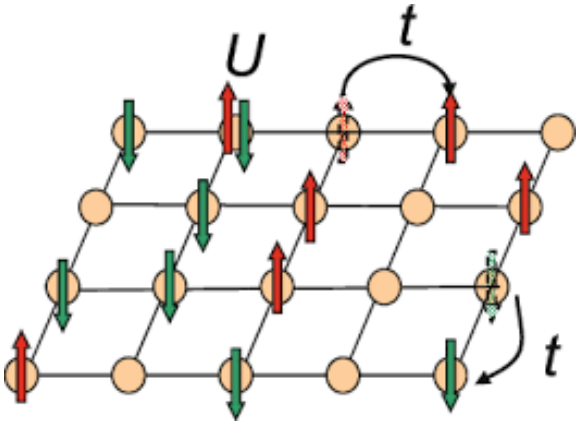
Generalities

- Nearly free electron and the tight – binding models (non – interacting electrons and static lattice)



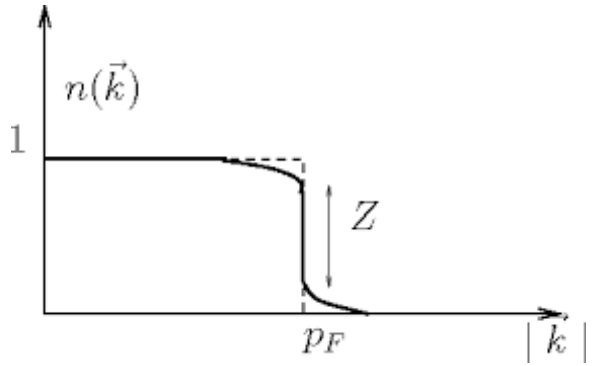


- Hubbard model (tight – binding plus on – site repulsion)

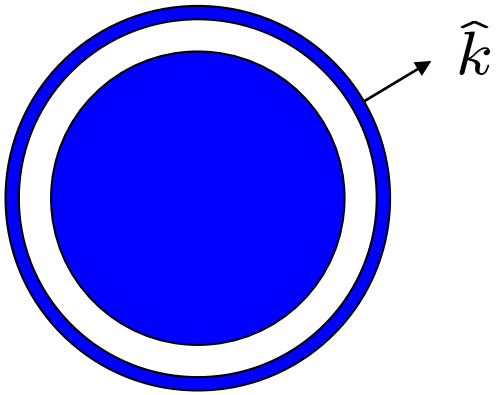


Generalities

- Landau's Fermi liquid theory (weakly interacting quasiparticles in a strongly interacting fermionic system; liquid ^{3}He)

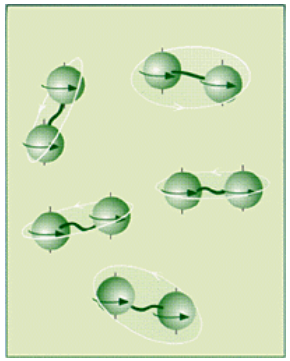


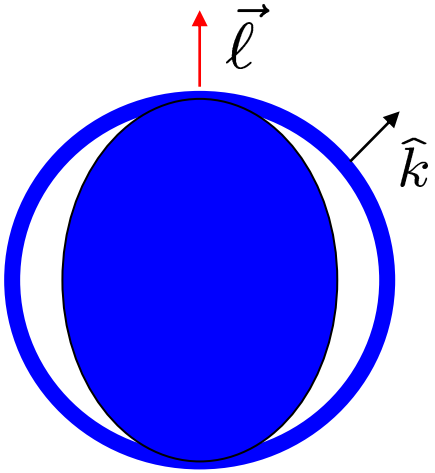
- BCS model for *s* – wave superconductivity (electronic pairing mediated by phonons in most superconducting metals)



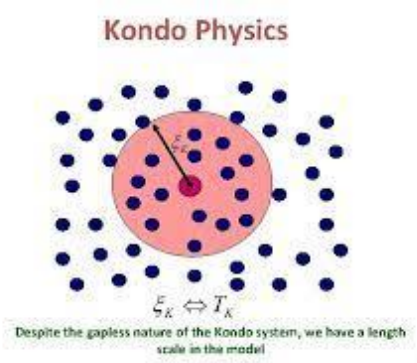
Generalities

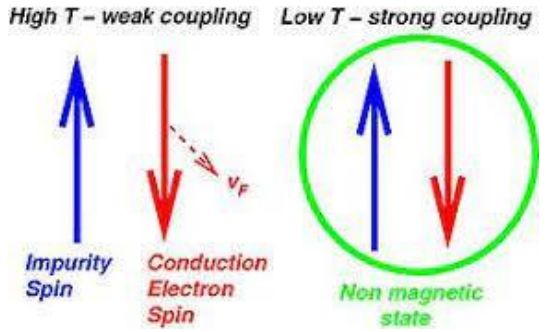
- BCS model for *p* – wave superconductivity (pairing of Landau's quasiparticles in superfluid ^{3}He via van der Waals attraction and spin fluctuation mechanism)





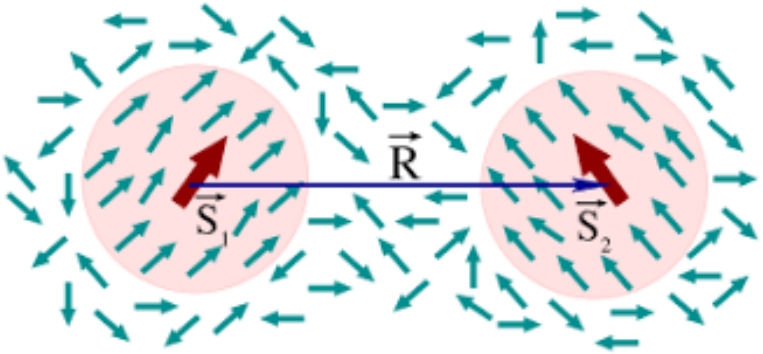
- Kondo model (magnetic impurity in a metal)



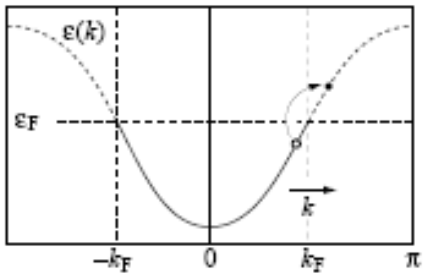


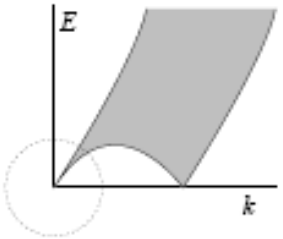
Generalities

- Kondo lattice (magnetic lattice in a metal; RKKY interaction)



- Bosonization: Luttinger liquid





- …
- is there room for more?
- Where?

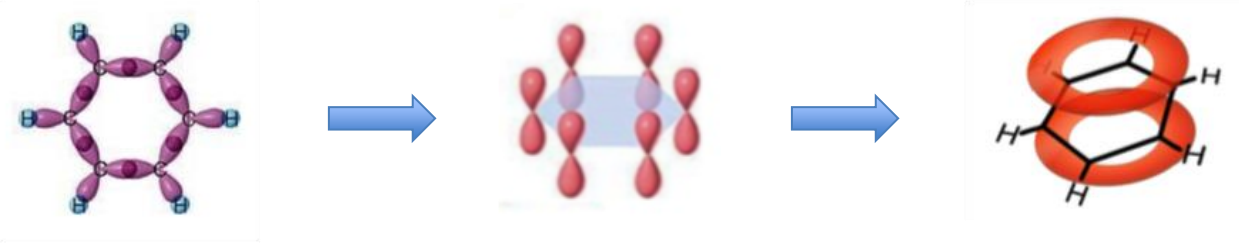
Motivation

Aromatic molecules exhibit large diamagnetic anisotropy when subject to external magnetic fields perpendicular to their basal plane

$$|\chi_{\perp}| > |\chi_{||}|$$

Pauling, Lonsdale and London: *Ring Current Model* (RCM)

Benzene:



$\Delta\chi_{RCM} = -4.92 \times 10^{-5}\mathrm{cm}^3/\mathrm{mol}$ $\Delta\chi_{exp} = -5.48 \times 10^{-5}\mathrm{cm}^3/\mathrm{mol}$

London: supracurrents (?)

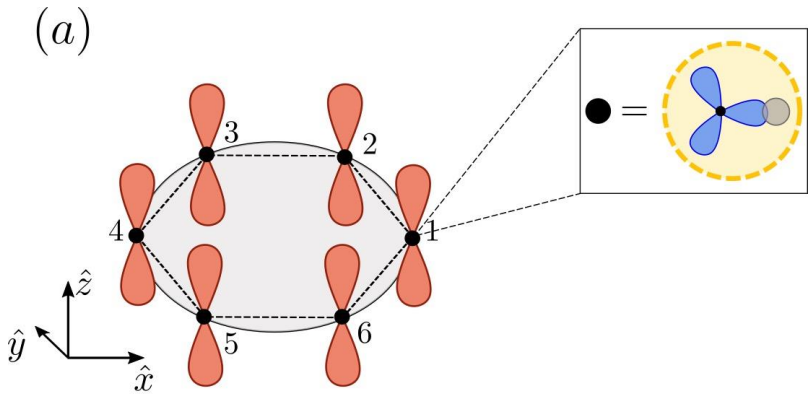
J. Chem. Phys. 5, 837 (1937)

More recently: Cooper pairing (?)

R. Wehlitz *et.al*. Phys. Rev. Lett. 109, 193001 (2012)

Model systems: the Hubbard rings

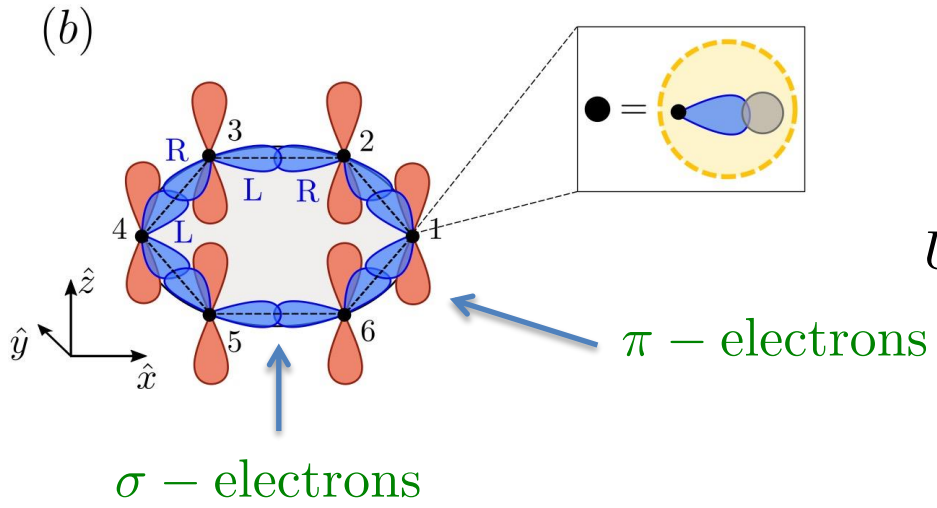
$$\boldsymbol{\mathcal{R}}_j = \frac{a}{\sqrt{2\left(1-\cos(2\pi/N)\right)}}\left[\cos\alpha_j\hat{\mathbf{x}} + \sin\alpha_j\hat{\mathbf{y}}\right]$$



N sites and N_e electrons

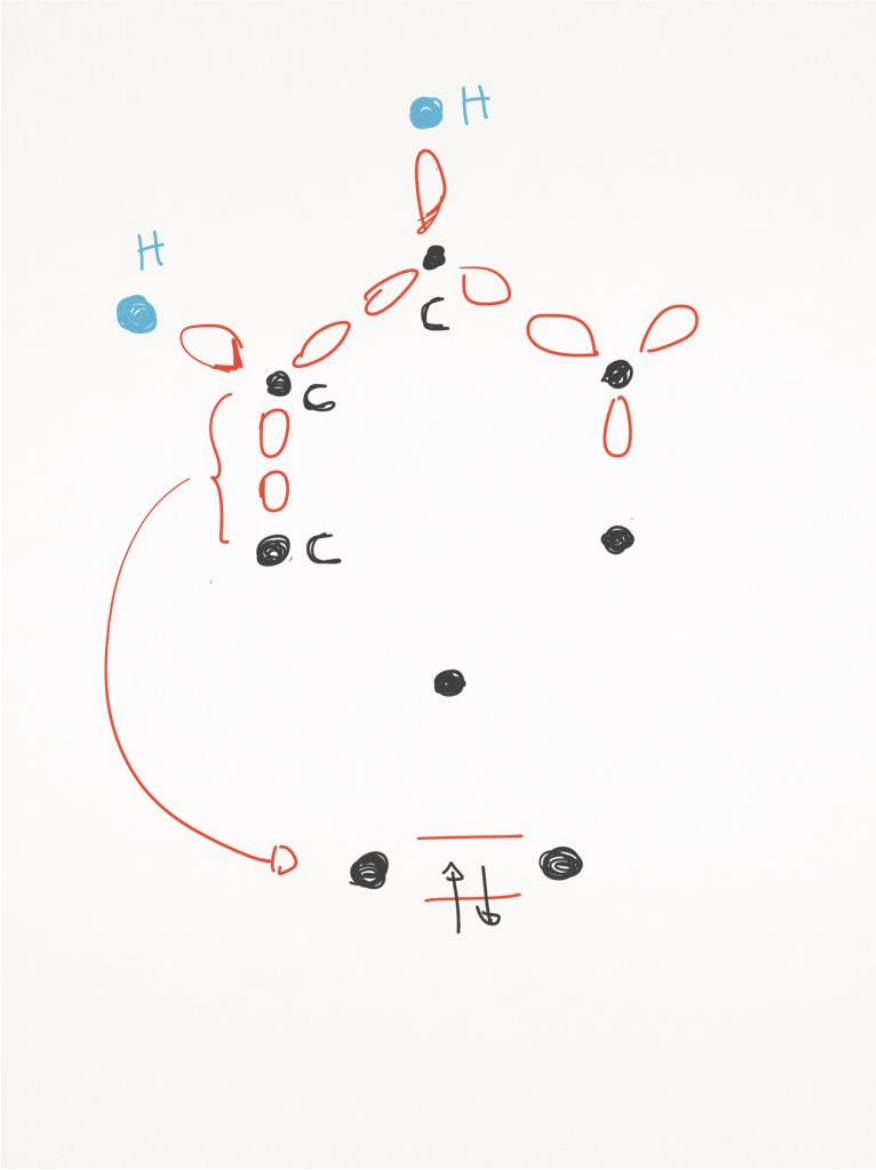
$$2s, 2p_x, 2p_y, \text{and } 2p_z$$
$$\rightarrow \quad 2sp^2, \text{ and } 2p_z$$

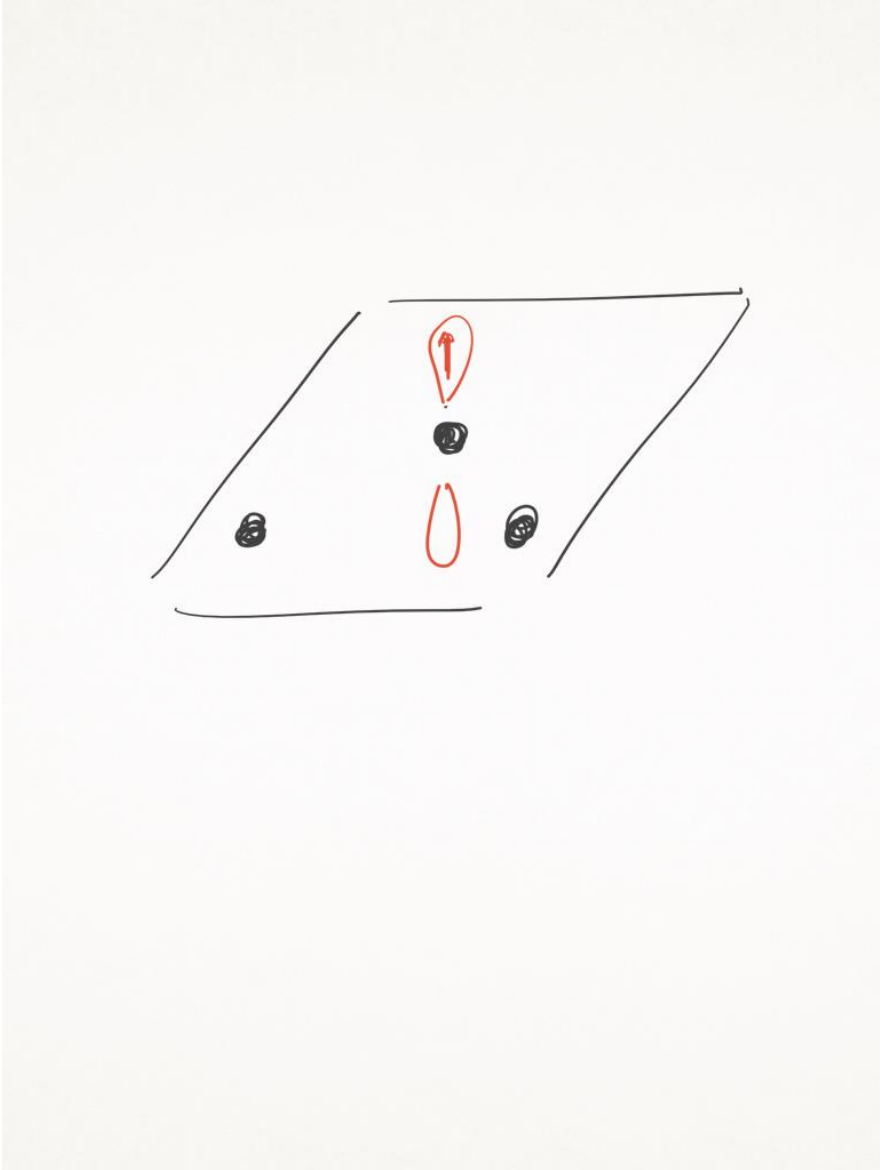
$$t = -\int d\mathbf{r}\, \varphi^*_{i+1}(\mathbf{r}) \left[-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V_c(\mathbf{r})\right] \varphi_i(\mathbf{r})$$



$$U = e^2 \int d\mathbf{r} \int d\mathbf{r}' \, \frac{|\varphi_i(\mathbf{r})|^2 \, |\varphi_i(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}$$

Model systems: the Hubbard rings





Model systems: the Hubbard rings

Hubbard model

$$\hat{H}_0 = -t \sum_{j=1}^{N} \sum_{\sigma} \left(c_{j\sigma}^{\dagger} c_{j+1\sigma} + \text{ h.c.} \right) + U \sum_{j=1}^{N} \hat{n}_{j\uparrow} \hat{n}_{j\downarrow}$$

$$c_{j\sigma}^{\dagger} = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} e^{-i2\pi kj/N} c_{k\sigma}^{\dagger} \quad \text{and} \quad c_{j\sigma} = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} e^{i2\pi kj/N} c_{k\sigma}$$

If $U = 0$ 

$$\hat{H}_{\text{Hückel}} = -2t \sum_{k=0}^{N-1} \sum_{\sigma=\uparrow,\downarrow} \cos\left(\frac{2\pi k}{N} \right) c_{k\sigma}^{\dagger} c_{k\sigma}$$

T. V. Trevisan, G. M. Monteiro, and A.O.C., Phys. Rev. B **103**, L180402 (2021)

Diamagnetism of benzene

We investigated the electric transport properties of small rings with $3 \leq N \leq 6$ sites and $N_e \leq N$ electrons

$$\hat{H} = -t \sum_{j=1}^{N} \sum_{\sigma=\uparrow,\downarrow} \left(c_{j\sigma}^{\dagger} c_{(j+1)\sigma} + h.c. \right) + U \sum_{j=1}^{N} \hat{n}_{j\uparrow} \hat{n}_{j\downarrow}$$

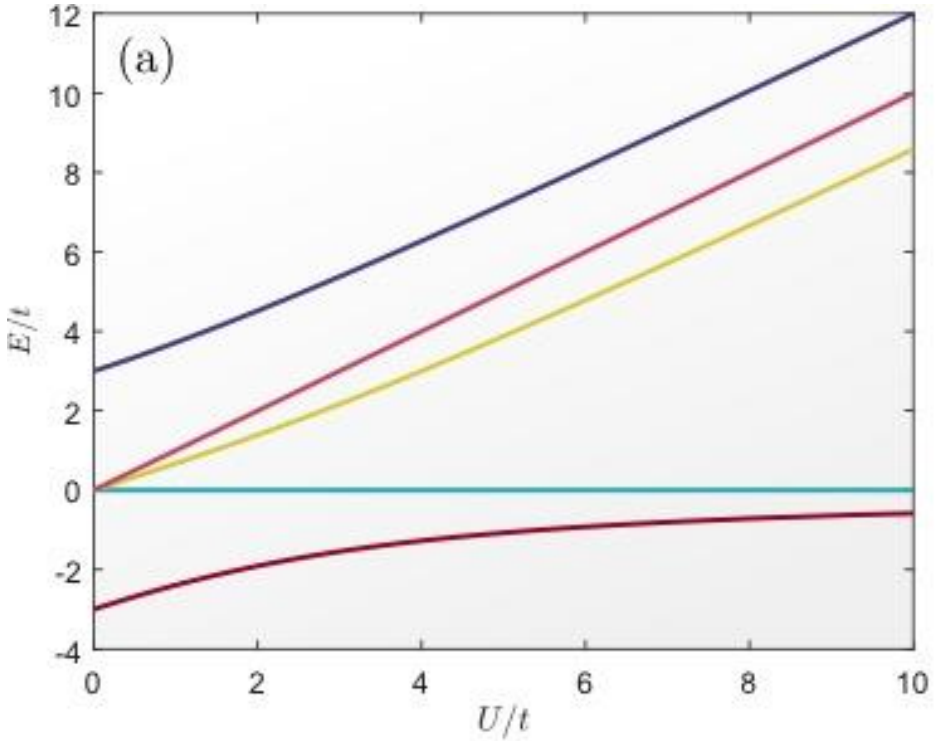
Exact diagonalization (numerical):

$$E_n^{(k)} \leftrightarrow \left\{ \left| \psi_n^{(k)} \right\rangle, k = 1, 2, \cdots, g_n \right\}$$

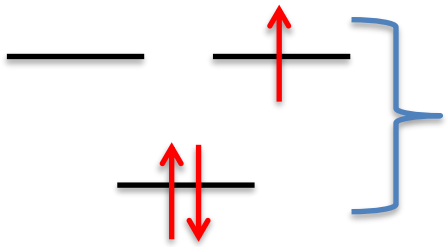
$$\updownarrow$$

$$g_n \geq 1$$

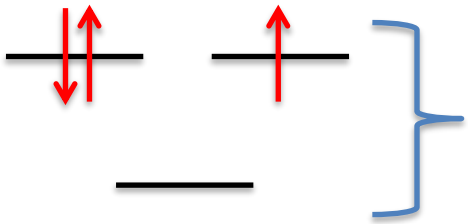
Our simplest example $N = N_e = 3$



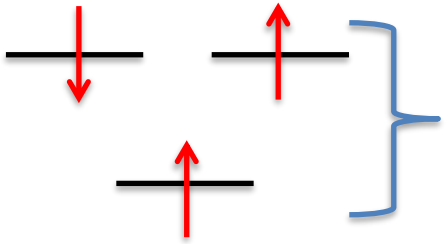
Non-interacting eigenstates



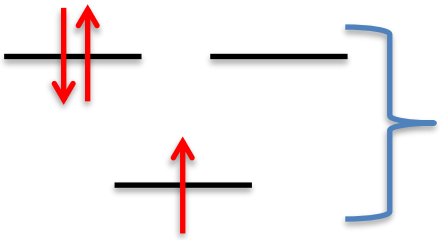
$g_0 = 4$



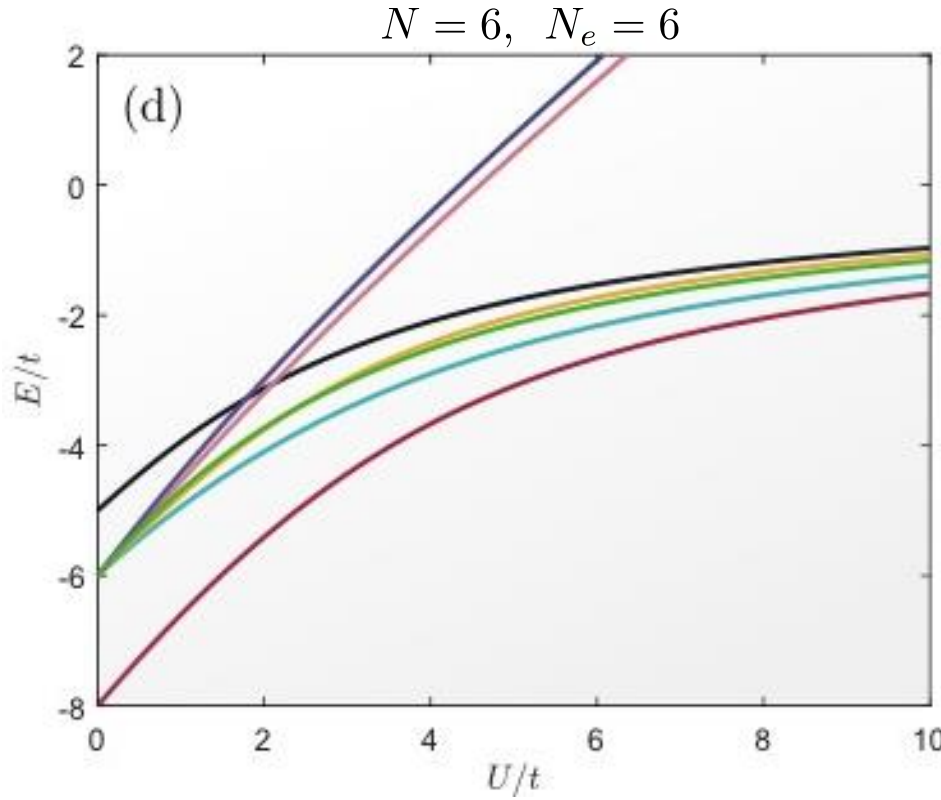
$g_3 = 4$



$g_1 = 8$



$g_2 = 4$



Characterization of the degenerate subspaces through the current operator

$$\hat{\mathcal{J}}_{el} = -\frac{iet}{N}\sum_{j=1}^{N}\sum_{\sigma}\left(c^{\dagger}_{j\sigma}c_{(j+1)\sigma} - c^{\dagger}_{(j+1)\sigma}c_{j\sigma}\right)$$

$$|\psi\rangle = \sum_{k=1}^{g_n} a_k \left|\psi_n^{(k)}\right\rangle$$

$\left\langle\psi\left|\hat{\mathcal{J}}_{el}\right|\psi\right\rangle = 0 \leftrightarrow$ subspace cannot support current carrying states

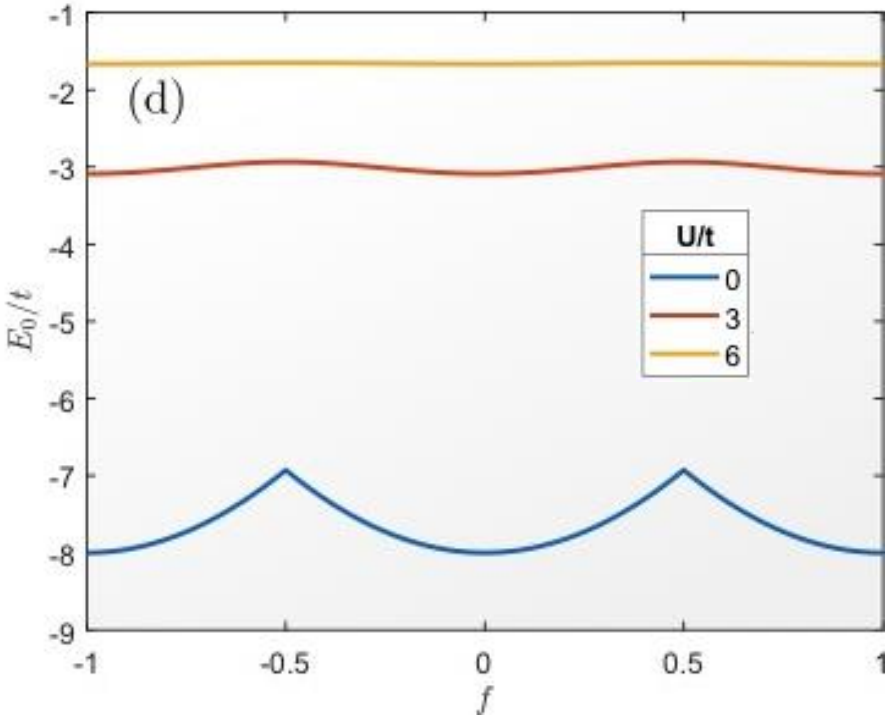
$\left\langle\psi\left|\hat{\mathcal{J}}_{el}\right|\psi\right\rangle \neq 0 \leftrightarrow$ subspace can support current carrying states

In the presence of an external field *B* ($f = \phi/\phi_0$ and $\phi_0 = hc/|e|$)

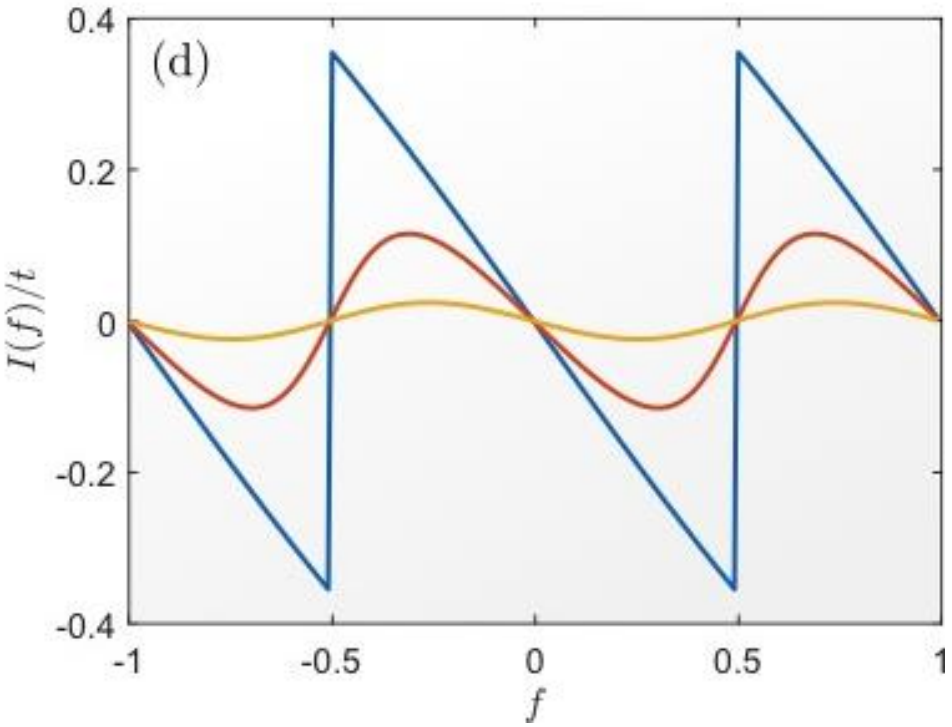
$$\hat{H} = -t\sum_{j=1}^{N}\sum_{\sigma}\left(e^{i2\pi f/N}c^{\dagger}_{j\sigma}c_{(j+1)\sigma} + h.c.\right) + U\sum_{j=1}^{N}\hat{n}_{j\uparrow}\hat{n}_{j\downarrow}$$

the persistent current in the ground state is $I(f) = -\frac{c}{\phi_0}\frac{\partial E_0}{\partial f}$

$N = 6,\ \ N_e = 6$



$N = 6,\ \ N_e = 6$

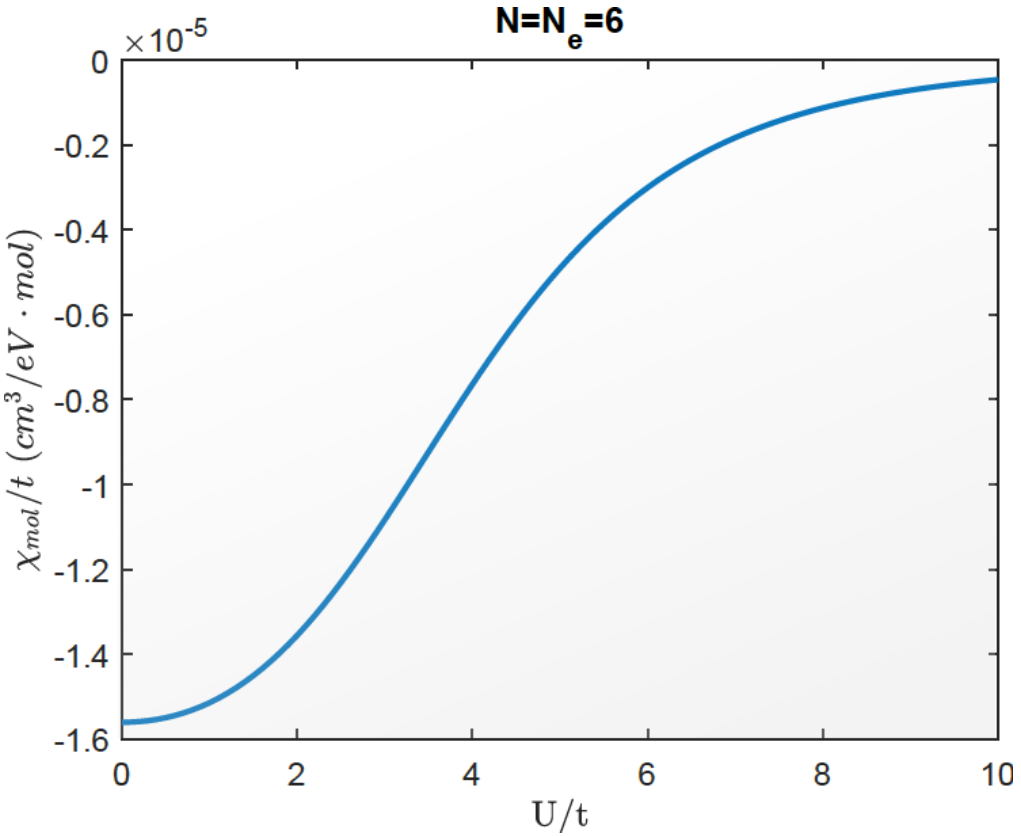


$$\Rightarrow \chi_{mag}^{(mol)} = N_A \chi = N_A \frac{N^4 a^4 e}{32\pi^3 \hbar c^2} \frac{\partial I(f)}{\partial f}$$

Benzene ($N = N_e = 6$): $t \approx 2.5\,\mathrm{eV}, a \approx 1.4\text{Å}$

$$\Rightarrow |\chi_{mag}^{(mol)}| = 1.9 \times 10^{-5}\mathrm{cm}^3/\mathrm{mol} < \Delta\chi_{RCM} < \Delta\chi_{exp}$$

$$\Delta\chi_{RCM} = -4.92 \times 10^{-5}\mathrm{cm}^3/\mathrm{mol} \qquad \Delta\chi_{exp} = -5.48 \times 10^{-5}\mathrm{cm}^3/\mathrm{mol}$$



Questions:

- RCM is certainly too naïve, but is the Hubbard model suitable to study the problem?
- What other effects should be included? Phonons? Next nearest neighbour interaction (Hubbard – V) ?
- What about the bonding electrons effects? How to incorporate them into the Hubbard scheme?

T. V. Trevisan, G. M. Monteiro, and A.O.C., Phys. Rev. B **102**, 125128 (2020)

Beyond B – O and the new effective interaction

Let us exemplify our explanation with the benzene molecule $\hat{H} = \hat{H}_p + \hat{H}_b$

Hamiltonian of the $\pi -$ electrons

$$\hat{H}_p = \sum_{i=1}^{N_\pi} \left(\frac{\mathbf{P}_i^2}{2m} + V_c(\mathbf{R}_i) \right) + \frac{1}{2} \sum_{i \neq j} U\left(\mathbf{R}_i - \mathbf{R}_i\right)$$

Hamiltonian of the $\sigma -$ electrons

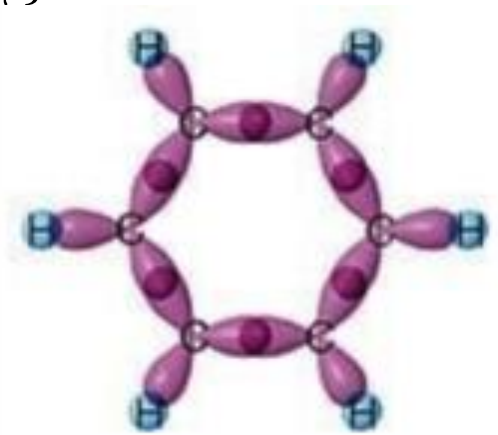
$$\hat{H}_b = \sum_{\alpha=1}^{N_\sigma} \left(\frac{\mathbf{p}_\alpha^2}{2m} + V_c(\mathbf{r}_\alpha) \right) + \frac{1}{2} \sum_{\alpha \neq \beta} U\left(\mathbf{r}_\alpha - \mathbf{r}_\beta\right) + \sum_{i,\alpha} U\left(\mathbf{r}_\alpha - \mathbf{R}_i\right)$$

$N_\pi = 6 \quad p_z -$ orbitals $\quad \mathbf{R} \equiv \{\mathbf{R}_1, \mathbf{R}_2, \cdots, \mathbf{R}_{N_\pi}\}$

$N_\sigma = 12 \quad sp_2 -$ orbitals $\quad \mathbf{r} \equiv \{\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_{N_\sigma}\}$

$V_c(\mathbf{r}) \leftrightarrow$ core (ionic) potential

$U\left(\mathbf{x} - \mathbf{x}'\right) \leftrightarrow$ interelectronic potential



We want to solve $\hat{H}\psi = E\psi$ with ions completely frozen

Born-Oppenheimer ansatz $\psi(\mathbf{r},\mathbf{R}) = \sum_{\nu} \phi_{\nu}(\mathbf{R})\,\varphi_{\nu}(\mathbf{r},\mathbf{R})$

where $\hat{H}_b(\mathbf{R})\varphi_{\nu}(\mathbf{r},\mathbf{R}) = \lambda_{\nu}(\mathbf{R})\varphi_{\nu}(\mathbf{r},\mathbf{R})$ with $\lambda_{\nu}(\mathbf{R}) = \lambda_{\nu}(\mathbf{R}_1,\mathbf{R}_2,\cdots,\mathbf{R}_{N_\pi})$

Full Schrödinger equation: $\pi-$ electrons slow and $\sigma-$ electrons fast

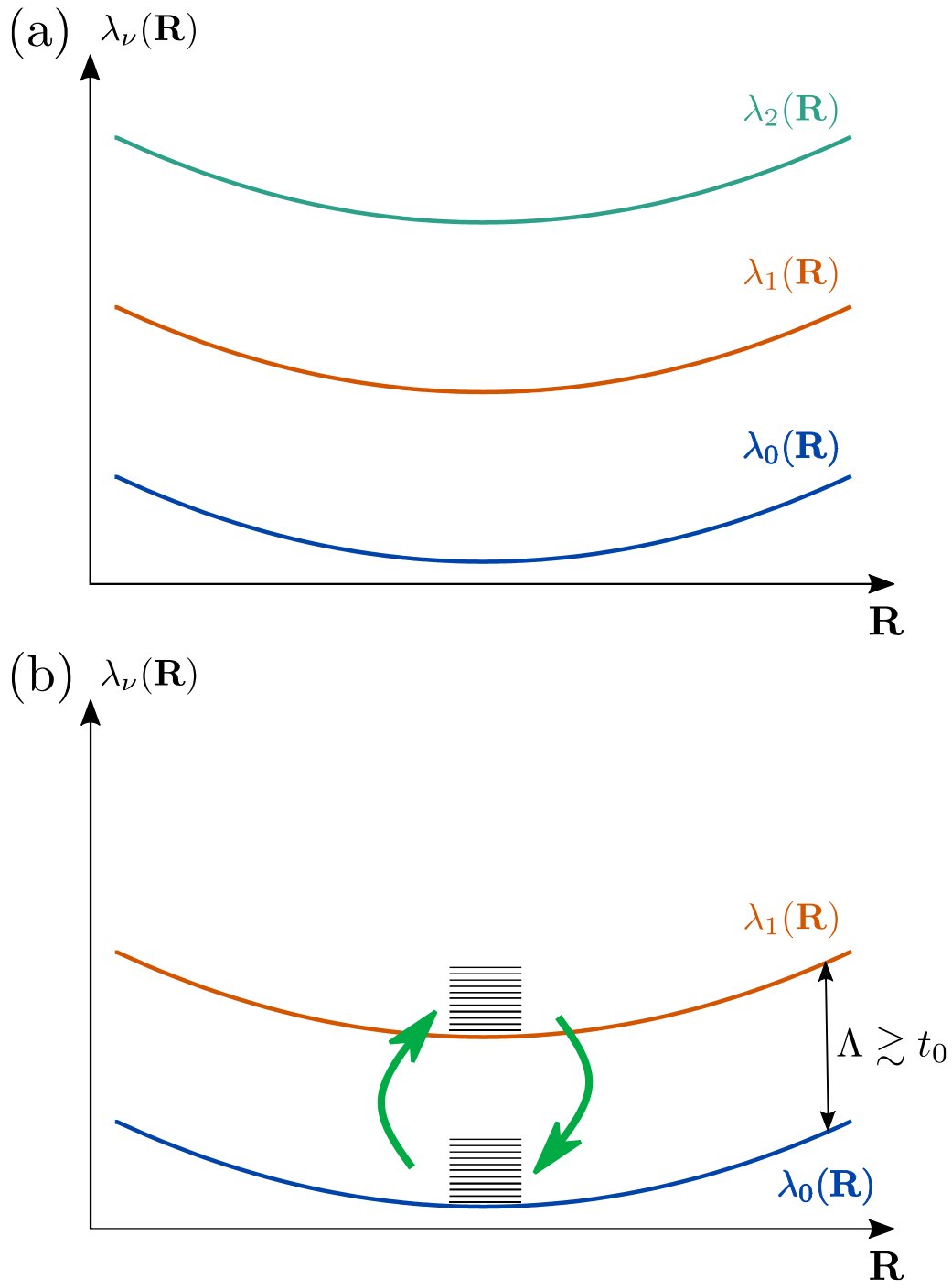
$$\sum_{\nu}\left\{\left[\hat{H}_p\phi_{\nu}(\mathbf{R}) + \lambda_{\nu}(\mathbf{R})\phi_{\nu}(\mathbf{R})\right]\varphi_{\nu}(\mathbf{r},\mathbf{R}) + \frac{1}{2m}\sum_{j=1}^{N_\pi}\left[\mathbf{P}_j^2\,\varphi_{\nu}(\mathbf{r},\mathbf{R}) + 2\left(\mathbf{P}_j\,\varphi_{\nu}(\mathbf{r},\mathbf{R})\right)\cdot\mathbf{P}_j\right]\phi_{\nu}(\mathbf{R})\right\}$$

$$= E\sum_{\nu}\phi_{\nu}(\mathbf{R})\varphi_{\nu}(\mathbf{r},\mathbf{R}) \quad \text{with} \quad \langle\varphi_{\mu}\,|\,\varphi_{\nu}\rangle_{\mathbf{r}} = \int d\mathbf{r}\,\varphi_{\mu}^{*}(\mathbf{r},\mathbf{R})\varphi_{\nu}(\mathbf{r},\mathbf{R}) = \delta_{\mu,\nu}$$

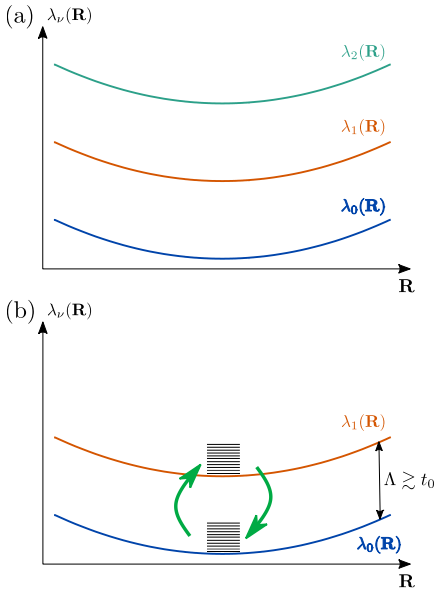
and $d\mathbf{r} = \prod_{\alpha=1}^{N_\sigma} d\mathbf{r}_{\alpha}$ ⇒ $\left[\hat{H}_p + \lambda_{\nu}(\mathbf{R})\right]\phi_{\nu}(\mathbf{R}) + \sum_{\mu} A_{\nu\mu}\phi_{\mu}(\mathbf{R}) = E\phi_{\nu}(\mathbf{R})$

$\nu = 0,1,2,\cdots$ $\qquad A_{\nu\mu} \equiv \left\langle \varphi_{\nu}\left|\sum_{j=1}^{N_\pi}\frac{\mathbf{P}_j^2}{2m}\right|\varphi_{\mu}\right\rangle_{\mathbf{r}} + \frac{1}{m}\sum_{j=1}^{N_\pi}\langle\varphi_{\nu}\,|\mathbf{P}_j|\,\varphi_{\mu}\rangle_{\mathbf{r}}\cdot\mathbf{P}_j$

$$\Lambda_{\mu\nu}(\mathbf{R}) \equiv \lambda_{\mu}(\mathbf{R}) - \lambda_{\nu}(\mathbf{R})$$


(a)
$\lambda_\nu(\mathbf{R})$
$\lambda_2(\mathbf{R})$
$\lambda_1(\mathbf{R})$
$\lambda_0(\mathbf{R})$
$\mathbf{R}$
(b)
$\lambda_\nu(\mathbf{R})$
$\lambda_1(\mathbf{R})$
$\Lambda \gtrsim t_0$
$\lambda_0(\mathbf{R})$
$\mathbf{R}$

Let us assume that only two subspaces are relevant $\psi(\mathbf{r},\mathbf{R}) = \phi_0(\mathbf{R})\varphi_0(\mathbf{r},\mathbf{R}) + \phi_1(\mathbf{R})\varphi_1(\mathbf{r},\mathbf{R})$



$$\begin{cases} \hat{H}_0\,\phi_{0,n}(\mathbf{R}) + A_{01}\,\phi_{1,n}(\mathbf{R}) = E_n\,\phi_{0,n}(\mathbf{R}) \\ \hat{H}_1\,\phi_{1,n}(\mathbf{R}) + A_{10}\,\phi_{0,n}(\mathbf{R}) = E_n\,\phi_{1,n}(\mathbf{R}) \end{cases}$$

where $\hat{H}_0 \equiv \hat{H}_p + \lambda_0(\mathbf{R})$ and $\hat{H}_1 \equiv \hat{H}_p + \lambda_1(\mathbf{R})$

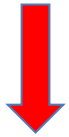
This gives $\left[\hat{H}_0 + A_{01}\left(E_n - \hat{H}_1\right)^{-1} A_{10}\right]\phi_{0,n}(\mathbf{R}) = E_n\,\phi_{0,n}(\mathbf{R})$

decoupled subspaces: adiabatic approximation

$$\begin{cases} \hat{H}_0\,\chi_{0,n}(\mathbf{R}) = \varepsilon_n^{(0)}\chi_{0,n}(\mathbf{R}) \ , \\ \hat{H}_1\,\chi_{1,n}(\mathbf{R}) = \varepsilon_n^{(1)}\chi_{1,n}(\mathbf{R}) \end{cases}$$

defining

$$\begin{cases} \left\langle \mathbf{R} \mid n^{(0)} \right\rangle \equiv \chi_{0,n}(\mathbf{R}) \qquad \left\langle \mathbf{R} \mid n^{(1)} \right\rangle \equiv \chi_{1,n}(\mathbf{R}) \\ \left\langle \mathbf{R} \mid N^{(0)} \right\rangle \equiv \phi_{0,n}(\mathbf{R}) \qquad \left\langle \mathbf{R} \mid N^{(1)} \right\rangle \equiv \phi_{1,n}(\mathbf{R}) \end{cases}$$



Wigner – Brillouin perturbation theory

$$\left|N^{(0)}\right\rangle \approx \left|n^{(0)}\right\rangle + \sum_{m\neq n} \frac{1}{\varepsilon_n^{(0)} - \varepsilon_m^{(0)}} \left\langle m^{(0)} \left| A_{01} \left(\varepsilon_n^{(0)} - \hat{H}_1\right)^{-1} A_{10} \right| n^{(0)} \right\rangle \left|m^{(0)}\right\rangle$$

$$W_{m,n} \equiv \left\langle m^{(0)} \left| W_{eff} \right| n^{(0)} \right\rangle \approx \left\langle m^{(0)} \left| A_{01} \left(\varepsilon_n^{(0)} - \hat{H}_1\right)^{-1} A_{10} \right| n^{(0)} \right\rangle$$

$$\mathbf{1} = \sum_n \left|n^{(1)}\right\rangle \left\langle n^{(1)}\right|$$

$$W_{eff} \approx -\frac{1}{\Lambda} A_{01} \mathcal{O} A_{10}$$

$$A_{\nu\mu} \equiv \left\langle \varphi_\nu \left| \sum_{j=1}^{N_\pi} \frac{\mathbf{P}_j^2}{2m} \right| \varphi_\mu \right\rangle_{\mathbf{r}} + \frac{1}{m} \sum_{j=1}^{N_\pi} \left\langle \varphi_\nu \left| \mathbf{P}_j \right| \varphi_\mu \right\rangle_{\mathbf{r}} \cdot \mathbf{P}_j$$

which can be approximated by $A_{\nu\mu} = -\frac{i\hbar}{ma}\frac{U}{\Lambda_{\mu\nu}}\sum_{j=1}^{N_\pi}\hat{n}_j \cdot \mathbf{P}_j$

$$W_{eff} = -\left(\frac{\hbar U}{ma}\right)^2 \frac{1}{\Lambda^3}\sum_{i\neq j=1}^{N_\pi}\hat{n}_i \cdot \mathbf{P}_i\,\mathcal{O}(\mathbf{R}_i,\mathbf{R}_j)\hat{n}_j \cdot \mathbf{P}_j$$

In second quantized form + localized orbitals representation for the electronic field operators:

$$\hat{W}_{eff} = -\lambda_N\left(\frac{U}{t}\right)^2\sum_{j=1}^{N}\sum_{\sigma,\sigma'}\Big[\left(c^\dagger_{j\sigma}c^\dagger_{j+1\sigma'}c_{j\sigma'}c_{j+1\sigma} + \text{h.c.}\right) + \\ + \left(c^\dagger_{j\sigma}c^\dagger_{j-1\sigma'}c_{j-2\sigma'}c_{j-1\sigma} + \text{h.c.}\right)\Big]$$

$$\lambda_N = \frac{t^4}{2\Lambda^3}\mathcal{O}_0\left[1-\cos\left(\frac{2\pi}{N}\right)\right]^2$$

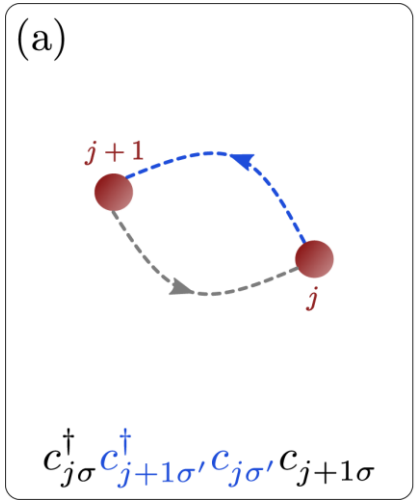
Extension of the Hubbard model

Let us study the Hamiltonian $\hat{H} = \hat{H}_{Hubbard} + \hat{H}_I$

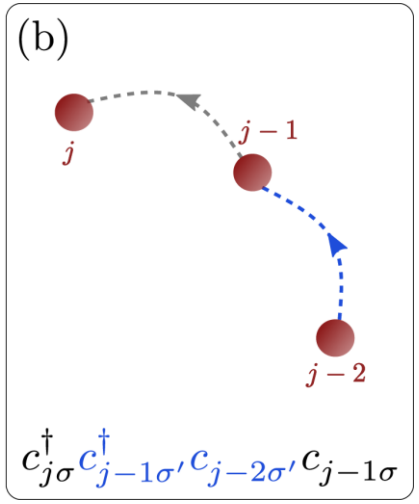
With the following extra interaction term ➡ (justified previously)

$$\hat{H}_I = -\lambda \left(\frac{U}{t}\right)^2 \sum_{j=1}^{N} \sum_{\sigma,\sigma'} \left[\left(c^\dagger_{j\sigma} c^\dagger_{j+1\sigma'} c_{j\sigma'} c_{j+1\sigma} + \text{h.c.} \right) + \left(c^\dagger_{j\sigma} c^\dagger_{j-1\sigma'} c_{j-2\sigma'} c_{j-1\sigma} + \text{h.c.} \right) \right]$$

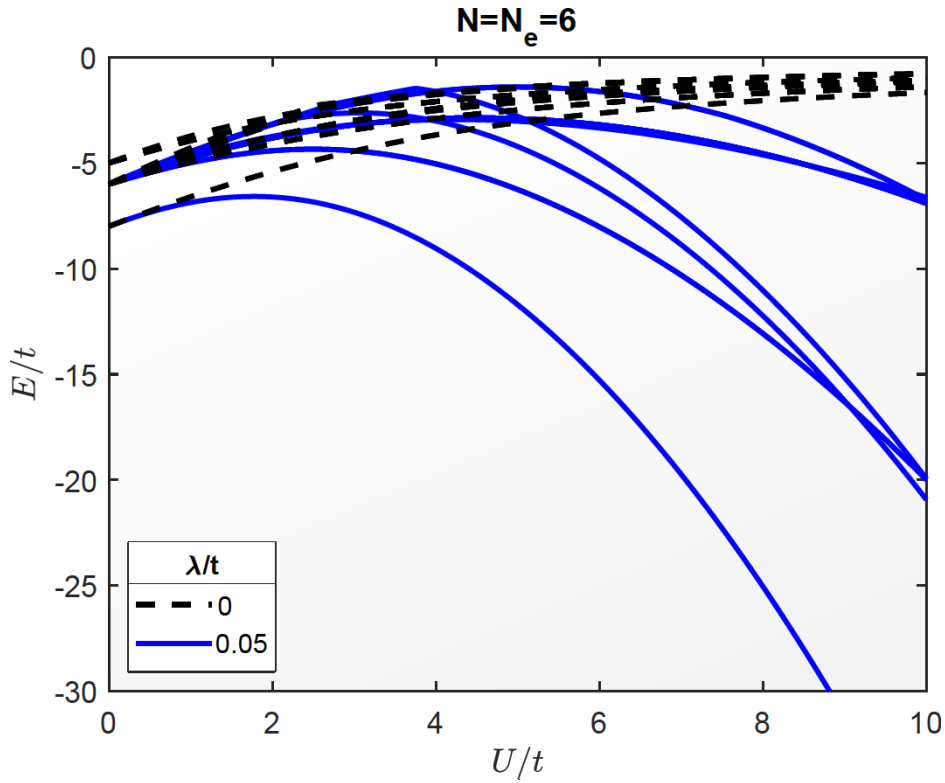
$$\lambda = \frac{t^4}{\Lambda^3}$$



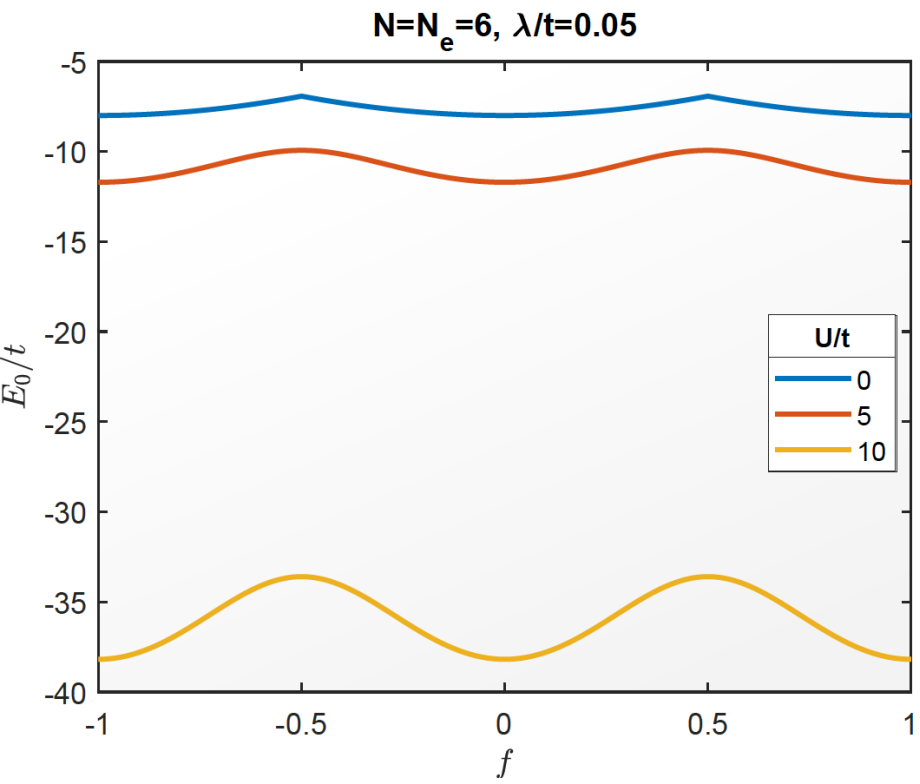
bubble

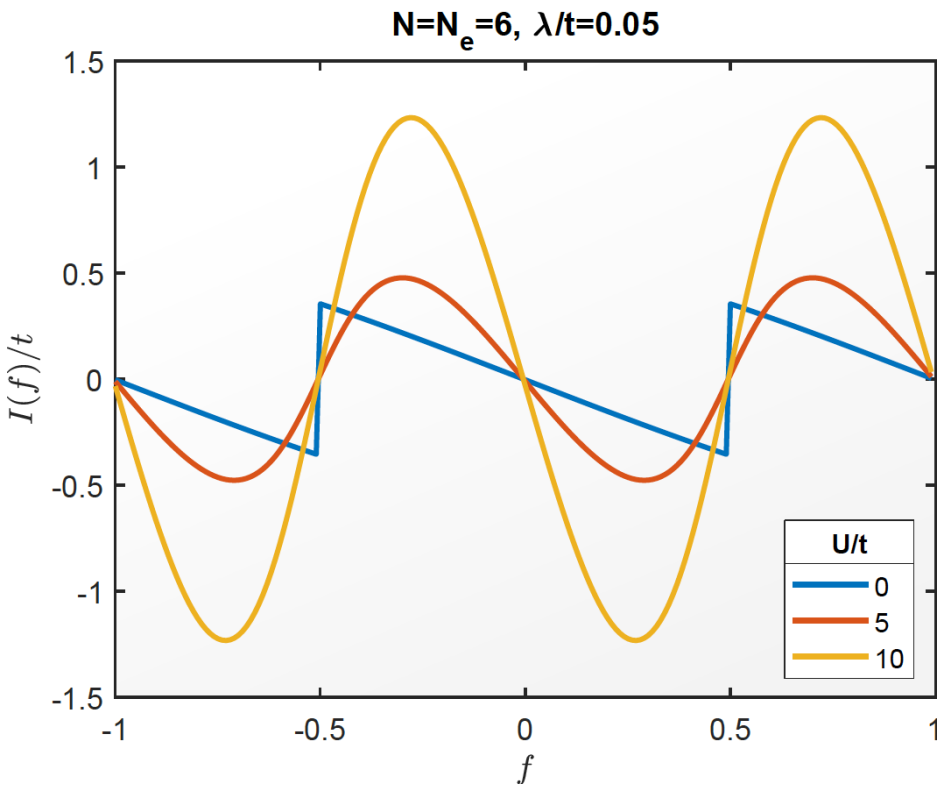


delocalized

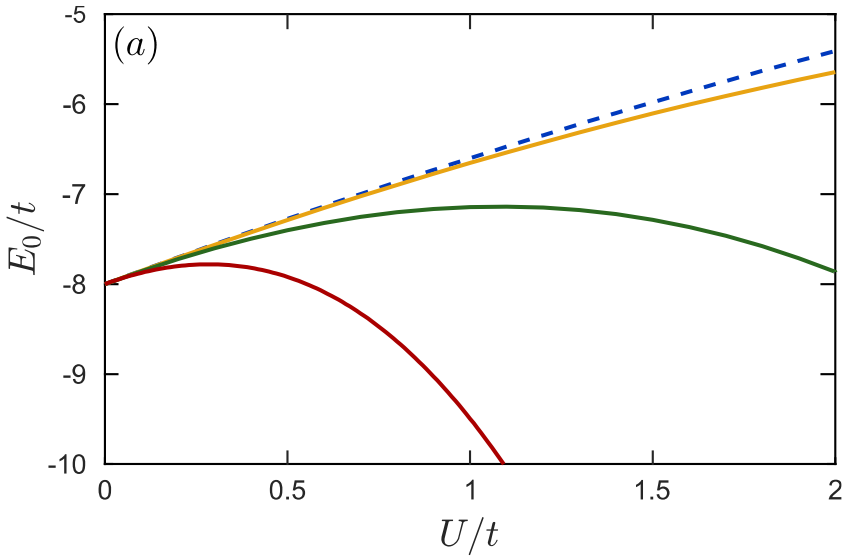


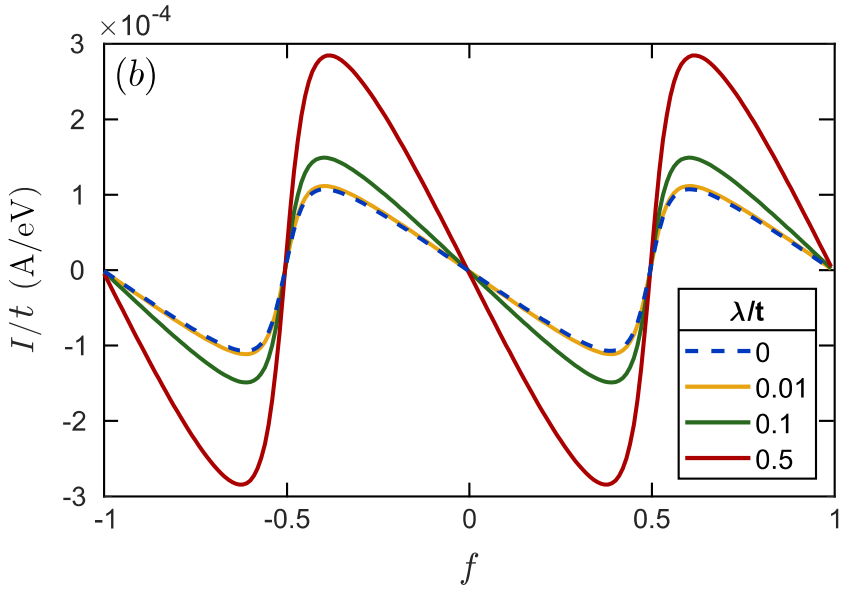
Ground state energy and current of the benzene molecule in a magnetic field





Ground state energy and current of the benzene molecule in a magnetic field



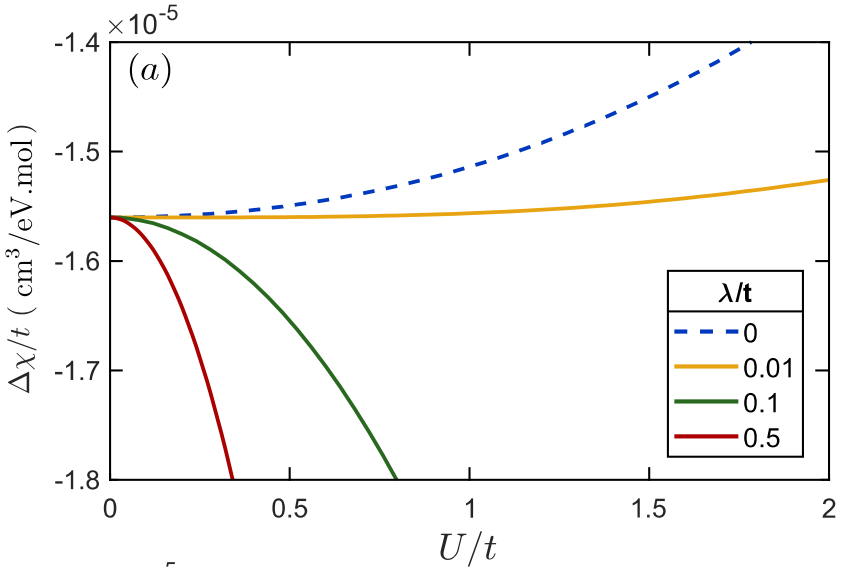


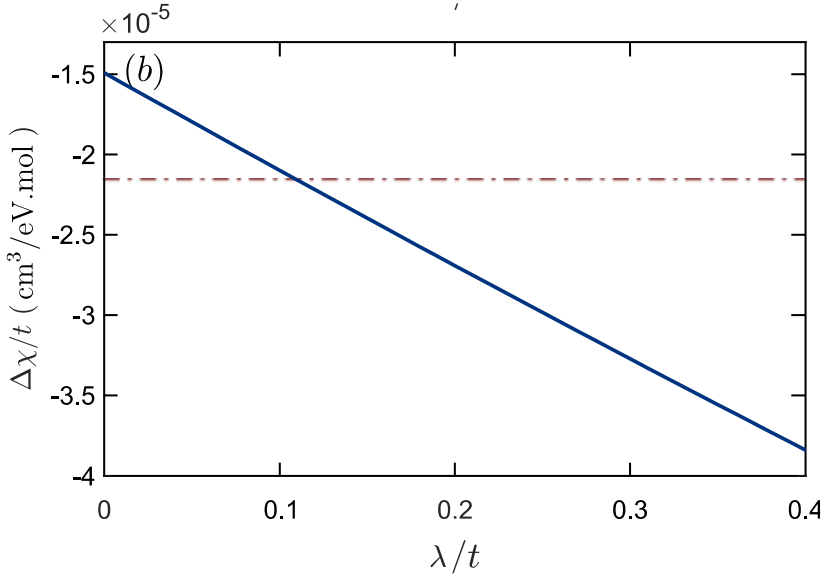
$t \approx 2.5\,\mathrm{eV},\ U/t = 1.2,\ a \approx 1.4\text{Å}$

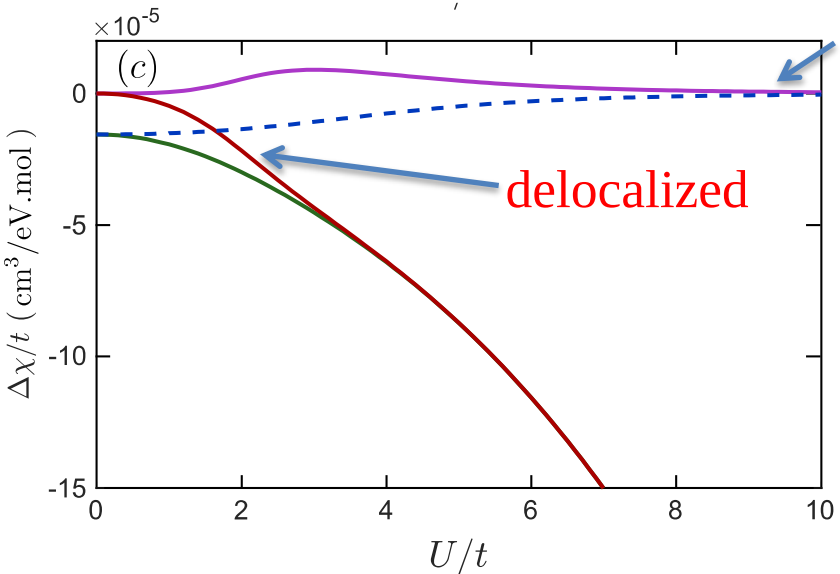
conditions for the validity of the extended model

$$\frac{t}{\Lambda} \lesssim 1 \qquad \frac{U}{t} < \left(\frac{t}{\Lambda}\right)^{\frac{3}{2}}$$

Magnetic susceptibility of the benzene molecule for various coupling parameters







$t \approx 2.5\,\mathrm{eV},\ U/t = 1.2,\ a \approx 1.4\text{Å}$

$$\frac{\Lambda}{t} \approx 2.1 \qquad \frac{\lambda}{t} \approx 0.11$$

Conclusions

Although the Hubbard model (good for narrow band systems) is not the most appropriate one for dealing with aromatic molecules, we have improved its applicability to these systems by adding an effective interaction between $\pi-$electrons which is mediated by virtual transitions of the binding $\sigma-$electrons. This new term;

a) makes the ground state energy of the molecule more negative for moderate values of U (pairing?),

b) provides us with more intense persistent currents in the ground state of the rings in the presence of external fields,

c) amplifies the diamagnetic response of these systems,

d) allows for a competition between diamagnetic and paramagnetic responses depending on the number of electrons and sites of the ring.

Comments

i) It would be desirable to test the present results with the ones predicted by more conventional ways to approach the electronic structure of molecules. For example, density functional theory. Are we accidentally selecting the most relevant part of the interelectronic interaction in the molecule for our specific purpose?

ii) Momentum – momentum coupling has appeared other times in the literature. The residual interelectronic interaction mediated by plasmons in the electron gas (Bohm and Pines, Phys. Rev. **92**, 609 (1953)), which is negligible due to the electronic screening, and the Breit – Darwin interaction which is a relativistic many – body effect are examples thereof.

iii) What about generalizations and/or applications to other low – dimensional carbon compounds?
Graphene ? Pyrolitic carbon (graphite) ? Cyclo[18]carbon?

iv) And to other low – dimensional strongly correlated electronic systems?

Thank you for your attention!