# SUPPLEMENTARY MATERIAL (2) FOR 'SECOND ORDER PERTURBATION THEORY TO DETERMINE THE MAGNETIC STATE OF FINITE SIZE AROMATIC HYDROCARBONS MOLECULES'

## 1 to set the number of azulene oligomers at the system

**Nsit defines the number of atoms at the system**

–> NumberOfOligomers: 2 $ Nsit : 10 + ( NumberOfOligomers - 1)*8; t: 1.$

*18*

## 2 to create a matrix, OliMatrix, for the non interacting Hamiltonian

–> modulo( a, b ) :=a - b*floor( a/b )$

–> OliMatrix:zeromatrix(Nsit, Nsit) $

–> for i: 1 thru Nsit do for j: 1 thru Nsit do if i-j = 1 and modulo(i,8)=7 then OliMatrix[i,j]:-t else if i-j = -1 and modulo(i,8) = 1 then OliMatrix[i,j]:-t else if i-j = 2 then OliMatrix[i,j]:-t;

–> auxMat:OliMatrix + transpose(OliMatrix)$ OliMatrix:auxMat$

## 3 compute the eiguenvalues and eigenvectors of the unperturbed system

–> load (lapack)$

–> eigenSys: dgeev ( OliMatrix ,True)$

–> eigenvalues: eigenSys[1]$

–> eigenvectors: transpose ( eigenSys[2] ) $

# 4 Tight-binding calculation for the electronic density of the non-perturbated system

–> orderedeigenvalues : sort (eigenvalues) $

**FermiGround defines the Fermi level, FermiP1 and FeermiM1 set the electronic filling for first excited state**

–> FermiGround : orderedeigenvalues[Nsit/2]; FermiP1 : orderedeigenvalues[Nsit/2 + 1]$ FermiM1 : orderedeigenvalues[Nsit/2 - 1]$

–> sitedensity (i, FermiLevel) := sum ( if eigenvalues[j] <= FermiLevel then eigenvectors[j][i]^2 else 0, j, 1, Nsit)$

–> density : makelist ( [ i , 2. * sitedensity(i,FermiGround)] , i, Nsit)$

**densDn and densUp compute respectively the density of electrons with spin up and down**

–> densDn : makelist ([ i , sitedensity(i,FermiM1)], i, Nsit)$ densUp : makelist ([ i , sitedensity(i,FermiP1)], i, Nsit)$

**densUpDnMs0 is density of electrons with spin up and down computed on Ms = 0 spin projections sub - spaces**

–> densUpDnMs0 : makelist ( sitedensity(i,FermiGround)*sitedensity(i,FermiGround), i, Nsit)$

**densUpDnMs1 is density of electrons with spin up and down computed on Ms = 1 spin projections sub - spaces**

–> densUpDnMs1 : makelist ( sitedensity(i,FermiP1)*sitedensity(i,FermiM1), i, Nsit)$

# 5 energies of the unperturbated system on Ms = 0 and Ms=1 spin projections sub - spaces

–> energyMs0 : 2. * sum ( if eigenvalues[j] <= FermiGround then eigenvalues[j] else 0, j, 1, Nsit);

$$-24.52188174203637$$

–> energyMs1 : energyMs0 + FermiP1 -FermiGround;

$$-24.01615315026958$$

# 6 First-Order Perturbation Theory for the Hubbard model on Ms=0 and Ms=1 spin projections sub-spaces

**Eq.(7) at SUPPLEMENTARY MATERIAL (1) computed on Ms=0 spin projections sub-spaces**

–> alfaMs0 : sum ( densUpDnMs0[i], i, 1, Nsit) - Nsit/2.;

$$-4.449986242244303$$

**Eq.(7) at SUPPLEMENTARY MATERIAL (1) computed on Ms=1 spin projections sub-spaces**

–> alfaMs1 : sum ( densUpDnMs1[i], i, 1, Nsit) - Nsit/2.;

$$-4.557368647201192$$

**Uc is the critical value of the electronic correlation for First-Order Perturbation Theory**

–> float ( solve ( [ Uc * ( alfaMs1 - alfaMs0 ) - ( energyMs1 - energyMs0)], [Uc]) ) ;

$$[Uc = -4.709603886873415]$$

# 7 Second-Order Perturbation Theory for the Hubbard model on Ms=0 spin projections sub-space

**SumBB is the numerator in Eq.(17) at supplementary material (1)**

–> SumBB (ppu,pu,ppd,pd) := if eigenvalues[ppu] <= FermiGround and eigenvalues[pu] > FermiGround and eigenvalues[ppd] <= FermiGround and eigenvalues[pd] > FermiGround then sum ( eigenvectors[ppu][j] * eigenvectors[pu][j] *eigenvectors[ppd][j]*eigenvectors[pd][j] , j, 1, Nsit) else 0$

**SumBB is the denominator in Eq.(17) at supplementary material (1)**

–> DeltaE (ppu, pu, ppd, pd) := if eigenvalues[ppu] <= FermiGround and eigenvalues[pu] > FermiGround and eigenvalues[ppd] <= FermiGround and eigenvalues[pd] > FermiGround then eigenvalues[pu] + eigenvalues[pd] - eigenvalues[ppu] - eigenvalues[ppd] else 10000 $

**To build a table, TableBBEner, for the fraction at Eq.(17 )**

–> array (TableBBEner, flonum, Nsit, Nsit, Nsit, Nsit,2);

–> for ppu: 1 thru Nsit do for pu: 1 thru Nsit do for ppd: 1 thru Nsit do for pd: 1 thru Nsit do TableBBEner[ppu,pu,ppd,pd,1]:SumBB(ppu, pu, ppd, pd)^2$

–> for ppu: 1 thru Nsit do for pu: 1 thru Nsit do for ppd: 1 thru Nsit do for pd: 1 thru Nsit do TableBBEner[ppu,pu,ppd,pd,2]:DeltaE(ppu, pu, ppd, pd)$

**Eq.(17) at supplementary material (1)**

–> beta0 : sum ( sum ( sum ( sum ( TableBBEner[ppu,pu,ppd,pd,1]/ TableBBEner[ppu,pu,ppd,pd,2], pd,1,Nsit) , ppd,1,Nsit), pu,1,Nsit) , ppu,1,Nsit)$

**DeltaEUp is the denominator in Eq.(18) at supplementary material (1)**

–> DeltaEUp (ppu, pu) := if eigenvalues[ppu] <= FermiGround and eigenvalues[pu] > FermiGround then eigenvalues[pu] - eigenvalues[ppu] else 10000$

**SumBBNd is the numerator in Eq.(18) at supplementary material(1)**

–> SumBBNd (ppu,pu) := if eigenvalues[ppu] <= FermiGround and eigenvalues[pu] > FermiGround then sum ( eigenvectors[ppu][j]*eigenvectors[pu][j]* 1./2. * density[j][2] , j, 1, Nsit) else 0$

**To build a table, TableBUNdEner, for the fraction at Eq.(18)**

–> array (TableBUNdEner, flonum, Nsit, Nsit,2)$

–> for ppu: 1 thru Nsit do for pu: 1 thru Nsit do TableBUNdEner[ppu,pu,1] : SumBBNd(ppu,pu)^2;

–> for ppu: 1 thru Nsit do for pu: 1 thru Nsit do TableBUNdEner[ppu,pu,2] : DeltaEUp(ppu, pu);

**Eq.(18) at supplementary material (1)**

–> betaUp : sum ( sum ( TableBUNdEner[ppu,pu,1]/ TableBUNdEner[ppu,pu,2], pu,1,Nsit) , ppu,1,Nsit)$

**Eq.(8) at SUPPLEMENTARY MATERIAL (1) computed on Ms=0 spin projections sub-spaces**

–> betaMs0 : (beta0+2*betaUp);

$$0.28447881854422$$

**EnergyU2Ms0 is the energy of the system computet at Ms = 0 spin projections sub - spaces by using second-order perturbation theory**

–> U : 1.0$

–> energyU2Ms0 : energyMs0+ alfaMs0*U-(betaMs0)*U^2;

$$-29.25634680282489$$

# 8 Second-Order Perturbation Theory for the Hubbard model on Ms=1 spin projections subspace

**SumBB is the numerator in Eq.(17) at supplementary material (1)**

–> SumBB (ppu,pu,ppd,pd) := if eigenvalues[ppu] <= FermiP1 and eigenvalues[pu] > FermiP1 and eigenvalues[ppd] < FermiGround and eigenvalues[pd] >= FermiGround then sum ( eigenvectors[ppu][j] * eigenvectors[pu][j] * eigenvectors[ppd][j] * eigenvectors[pd][j] , j, 1, Nsit) else 0$

**SumBB is the denominator in Eq.(17) at supplementary material (1)**

–> DeltaE (ppu, pu, ppd, pd) := if eigenvalues[ppu] <= FermiP1 and eigenvalues[pu] > FermiP1 and eigenvalues[ppd] < FermiGround and eigenvalues[pd] >= FermiGround then eigenvalues[pu] + eigenvalues[pd] - eigenvalues[ppu] - eigenvalues[ppd] else 10000$

**To build a table, TableBBEner, for the fraction at Eq.(17)**

–> array (TableBBEner, flonum, Nsit, Nsit, Nsit, Nsit,2)$

–> for ppu: 1 thru Nsit do for pu: 1 thru Nsit do for ppd: 1 thru Nsit do for pd: 1 thru Nsit do TableBBEner[ppu,pu,ppd,pd,1]:SumBB(ppu, pu, ppd, pd)^2;

–> for ppu: 1 thru Nsit do for pu: 1 thru Nsit do for ppd: 1 thru Nsit do for pd: 1 thru Nsit do TableBBEner[ppu,pu,ppd,pd,2]:DeltaE(ppu, pu, ppd, pd);

**Eq.(17) at supplementary material (1)**

–> beta0 : sum ( sum ( sum ( sum ( TableBBEner[ppu,pu,ppd,pd,1]/ TableBBEner[ppu,pu,ppd,pd,2], pd,1,Nsit) , ppd,1,Nsit), pu,1,Nsit) , ppu,1,Nsit);

**SumBB is the denominator in Eq.(18) at supplementary material (1)**

–> DeltaEUp (ppu, pu) := if eigenvalues[ppu] <= FermiP1 and eigenvalues[pu] > FermiP1 then eigenvalues[pu] - eigenvalues[ppu] else 10000$

**SumBB is the numerator in Eq.(18) at supplementary material (1)**

–> SumBBNd (ppu,pu) := if eigenvalues[ppu] <= FermiP1 and eigenvalues[pu] > FermiP1 then sum ( eigenvectors[ppu][j]*eigenvectors[pu][j]*densDn[j][2] , j, 1, Nsit) else 0$

**To build a table, TableBUNdEner, for the fraction at Eq.(18 )**

–> array (TableBUNdEner, flonum, Nsit, Nsit,2);

–> for ppu: 1 thru Nsit do for pu: 1 thru Nsit do TableBUNdEner[ppu,pu,1]:SumBBNd(ppu,pu)^2;

–> for ppu: 1 thru Nsit do for pu: 1 thru Nsit do TableBUNdEner[ppu,pu,2]:DeltaEUp(ppu, pu);

**Eq.(18) at supplementary material (1)**

–> betaUp : sum ( sum ( TableBUNdEner[ppu,pu,1]/ TableBUNdEner[ppu,pu,2], pu,1,Nsit) , ppu,1,Nsit);

**SumBB is the denominator in Eq.(19) at supplementary material (1)**

–> DeltaEdown (ppd, pd) := if eigenvalues[ppd] < FermiGround and eigenvalues[pd] >= FermiGround then eigenvalues[pd] - eigenvalues[ppd] else 10000$

**SumBB is the numerator in Eq.(19) at supplementary material (1)**

–> SumBBNu (ppd,pd) := if eigenvalues[ppd] < FermiGround and eigenvalues[pd] >= FermiGround then sum ( eigenvectors[ppd][j]*eigenvectors[pd][j]*densUp[j][2] , j, 1, Nsit) else 0$

**To build a table, TableBUNuEner, for the fraction at Eq.(19)**

–> array (TableBUNuEner, flonum, Nsit, Nsit,2)$

–> for ppd: 1 thru Nsit do for pd: 1 thru Nsit do TableBUNuEner[ppd,pd,1]:SumBBNu(ppd,pd)^2;

–> for ppd: 1 thru Nsit do for pd: 1 thru Nsit do TableBUNuEner[ppd,pd,2]:DeltaEdown(ppd, pd);

**Eq.(19) at supplementary material (1)**

–> betaDn : sum ( sum ( TableBUNuEner[ppd,pd,1]/ TableBUNuEner[ppd,pd,2], pd,1,Nsit) , ppd,1,Nsit)$

**Eq.(8) at SUPPLEMENTARY MATERIAL (1) computed on Ms=1 spin projections sub-spaces**

–> betaMs1 : (beta0+betaUp+betaDn);

*0.27116767746926*

**EnergyU2Ms1 is the energy of the system computed at Ms = 1 spin projections sub - spaces by using second-order perturbation theory**

–> U : 1.0$

–> energyU2Ms1 : energyMs1+ alfaMs1*U-(betaMs1)*U*U;

$$-28.84468947494004$$

# 9 Uc calculations for second-order Perturbation theory

**Uc is the ritical value of the electronic correlation U obtained with Second-Order Perturbation Theory**

–> float ( solve ( [ - (betaMs1 - betaMs0) * Uc2^2 + ( alfaMs1 - alfaMs0 ) * Uc2 + (energyMs1 - energyMs0)], [Uc2]) ) ;

$$[Uc2 = -5.1514829323009861^{-23}\ \left(9.0475477503885631^{22}\%i - 7.8298885269561681^{22}\right)$$

$$Uc2 = 5.1514829323009861^{-23}\ \left(9.0475477503885631^{22}\%i + 7.8298885269561671^{22}\right)]$$

–> wxplot2d([-( betaMs1 - betaMs0 ) * x^2 + ( alfaMs1 - alfaMs0 ) * x + (energyMs1 - energyMs0) ], [x,0,5], [y,0,0.5], [box, false], [label, ["x", 5.2, 0.], [ "Spin Gap", -1.6, .3 ]] )$

plot2d: some values were clipped.