Computation of Non-linear Magnetoelectric Coefficients for Low Dimensional Systems and Development of a few Quantum Many Body Methods

A Thesis
Submitted for Partial Fulfilment of the Degree of
Master of Science
as part of Intergrated PhD Programme

by
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April 2016

Dedicated to

my mentors

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DECLARATION

I hereby declare that the matter embodied in the thesis entitled "**Computation of Non-linear Magnetoelectric Coefficients for Low Dimensional Systems and Development of a few Quantum Many Body Methods**" is the result of investigations carried out by me at the Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India under the supervision of Prof. Swapan K. Pati and that it has not been submitted elsewhere for the award of any degree or diploma.

In keeping with the general practice in reporting scientific observations, due acknowledgement has been made whenever the work described is based on the findings of other investigators.

Abhiroop Lahiri

CERTIFICATE

I hereby certify that the matter embodied in this thesis entitled "**Computation of Non-linear Magnetoelectric Coefficients for Low Dimensional Systems and Development of a few Quantum Many Body Methods**" has been carried out by . Mr. Abhiroop Lahiri at the Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India under my supervision and that it has not been submitted elsewhere for the award of any degree or diploma.

(Prof. Swapan K. Pati
(Research Supervisor)

Acknowledgements

There are very few people who have achieved anything in their life without the support of anyone . I have got tremendous support from my father Dr. Anjan Kumar Lahiri and mother Mrs. Mandira Lahiri. They have always been there for me in whichever situation I was in, be it happy, sad, excited, bored, angry, hopeless and all the adjectives which have described me at different times. They have helped me at every second to become what I am now. I can't express in words how I am thankful to both the guide and the 'person' Swapan K. Pati. Not only he has guided me to do research, he has always taken care of me like my father when I am 1200 miles away from my parents. I also express my heartiest thanks Anusooya Pati who has cared me like my mother. I am indebted to Pandit Ajoy Chakraborty for constant guidance for 13 years and making music an integral part of my life, without which I could not have made the smallest achievement. I heartily thank Uday *Mama* for making me realize my slightest analytic skills, however small they may be. I express my gratitude to Mr. Patha Pratim Roy who has taught and motivated and inspired me at every moment in my journey of science till now. I sincerely thank all the CPMU and TSU faculty members who have not only guided me through the coursework ansd also helped me feel JNC to be my second home. And, now I can describe my labmates in one word. They are AWESOME ! I thank CPMU batchmates Nikita and Priyank for supporting me constantly for the last 3 years. Finally, I thank all my friends and all the JNC staff.

Contents

1

Introduction

Low dimensional systems have got tremendous impetus in last few decades due to their interesting and exotic properties. These properties arise when one or more spatial dimensions are reduced to less than a nanometre.This is because, the motion of electrons become contstrained along the reduced dimensions, when quantum confinement effects[1–7] begin to dominate. In fact, due to such effects, we have two-dimensional, one-dimensional and zero-dimensional systems which give rise to exotic properties[8–12]. Examples of such systems are many, including some of the famous ones being, fullerene, nanotubes, graphene etc. Nowadays, with the advent of synthesis and characterization techniques, there are realization of newer and newer low-dimensional systems almost in everyday basis.

Low dimensional systems are unique, in the sense that, in these systems, there is no long range order. In fact, there are several celebrated theorems which dictate the physics of low-dimensional systems. Most often, these systems are insulators, for many reasons, including lattice vibrations and electron correlations, leading to Peierls insulators and Mott insulators, respectively.The correlation functions decay exponentially with distance, which in turn induces a finite electronic gap in the low energy spectrun of these systems.

Quite often, in these systems, the electron electron interactions are very strong; such systems then are called strongly correlated systems. These systems show some exotic properties due to strong correlations. The absence of long range order is mainly due to quantum fluctuations. And if the quantum fluctulations are quite strong, it can induce spin-charge separation in low-dimensional systems. Most often, we find electronic system, where magnetic interactions dominate, while the system is a charge insulator. We have systems, like antiferromagnetic insulator and ferromagnetic metal. Interestingly, there are many broken symmetry phases, like spin density wave (SDW), charge density wave (CDW), bond order wave (BOW), superconductivity, superfluidity etc. which are often seen in low-dimensional systems.

With aplication of electric field, low dimensional systems give rise to a host of linear and non-linear optical properties, which are of importance in all optical computing to optical memory devices and fibers[13]. In general, a system shows Stark effect, which is non-linear, when electric field is applied, while it shows Zeeman splitting, which is linear, when subjected to a magnetic field. There have been enormous studies in the literature on linear and non-linear optical absorptions and emissions on a large number of systems with differing dimensionality. There are also many studies on modulating magnetic phenomena for applications in magnetic switches to magnetic recording with application of magnetic field. Thus, there exists a host of systems whose properties can be modulated for various application purposes by applying external electric field and magnetic fields. However, there have been almost no study on the effect of electric and magnetic field simultaneously on low dimensional correlated systems. This is because, such an effect will depend independently on the strength and direction of both electric and magnetic fields. Experimentally also there is hardly any work in this direction, as the setup would involve Z-scan method which is quite complicated.

1.1 Lattice Hamiltonians

In quantum mechanics, the Schrödinger equation can be written in general as

$$H\Psi = E\Psi$$

For a system with n electrons and N nuclei, the complete Hamiltonian H can be written as

$$\begin{aligned} H \;=\; & \frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\hat{\nabla}_i^{\,2} + \hbar^2\sum_{I=1}^{N}\frac{\hat{\nabla}_I^{\,2}}{2M_I} - \sum_{i=1}^{n}\sum_{I=1}^{N}\frac{Z_I e^2}{|\vec{r_i}-\vec{R_I}|} + \sum_{i=1}^{n}\sum_{j=i+1}^{n}\frac{e^2}{|\vec{r_i}-\vec{r_j}|} \\ & + \sum_{I=1}^{N}\sum_{J=I+1}^{N}\frac{e^2}{|\vec{R_I}-\vec{R_J}|} \end{aligned} \tag{1.1}$$

where i, j are the indices for the electrons and I, J are those for the nuclei. Similarly, r_i, r_j and R_I, R_J correspond to the coordinates of the electrons and nuclei respectively. The first 2 terms are the kinetic energies of the electrons and the nuclei. The others are respectively the electron-nucleus, electron-electron and the nucleus-nucleus interaction terms.

Born-Oppenheimer approximation allows us to separate the motion of the electrons and the nuclei, as the mass of the nuclei, M_I are very heavy compared to the m_e, the mass of the electrons and hence their configurational change can be considered negligible compared to the motion of the electrons.

Moreover, the nucleus-nucleus interaction terms do not affect the motion of the electrons. Hence their interaction energy can be directly added to the resulting energy eigenvalues of the electronic Hamiltonian. So we can omit those 2 terms from the total Hamiltonian. Finally, we omit the electron-nucleus interaction also, as it is a single-electron term and can be obtained after solving the electronic Hamiltonian, for fixed coordinates of the nuclei. Assuming only the electonic degrees of freedom with fixed nuclear coordinates, we can write the Hamiltonian terms involving the kinetic energy and the electron-electron interacton terms as,

$$H = \frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\hat{\nabla}_i^{\,2} + \sum_{i=1}^{n}\sum_{j=i+1}^{n}\frac{e^2}{|\vec{r_i}-\vec{r_j}|} \tag{1.2}$$

Fock Space

To treat the systems quantum mechanically, we need to start with a basis set. Due to the correlation between the electrons, we cannot take single electron wave functions as basis states. We have to treat the full system with certain configurations as basis states. the space of configurations is called the Fock space. For example, if we have a system of 2 sites (2 orbitals) with 2 electrons (half-filling), the Fock Space consists of the 6 possible configurations:

$$\begin{array}{ccc} \underline{\uparrow\ \uparrow} & \underline{\uparrow\ \downarrow} & \underline{\downarrow\ \uparrow} \\ \underline{\mathbf{0}\ \ \uparrow\downarrow} & \underline{\uparrow\downarrow\ \ \mathbf{0}} & \underline{\downarrow\ \downarrow} \end{array}$$

It is convinient to write the many-electron system in second-quantized notation as

$$H = -t\sum_{\langle ij,\rangle\sigma}\left\{c_{i\sigma}{}^{\dagger}c_{j\sigma} + h.c.\right\} + U\sum_{i} n_{i\uparrow}n_{i\downarrow} + \sum_{ijkl} V_{ijkl}c_{i\sigma}{}^{\dagger}c_{j\sigma}{}^{\dagger}c_{k\sigma}c_{l\sigma} \tag{1.3}$$

$c^{\dagger}_{i\sigma}$ and $c_{i\sigma}$ are respectively the creation and annihilation operators for an electron of spin σ=↑ or ↓ at site i.
$n_{i\sigma} \;=\; c^{\dagger}_{i\sigma}c_{i\sigma}$ is the number operator for site i.

In the Zero Differential Overlap approximation, there exist interaction terms only when their charge density of a electron is completely localized in one site or the other. Thus we have

$$V_{ijkl}c_{i\sigma}{}^{\dagger}c_{j\sigma}{}^{\dagger}c_{k\sigma}c_{l\sigma} \;\longrightarrow\; \delta_{ij}\delta_{kl}V_{ijkl}c_{i\sigma}{}^{\dagger}c_{j\sigma}{}^{\dagger}c_{k\sigma}c_{l\sigma}$$

that is, the terms having $i \neq \jmath$ and $k \neq l$ are not considered. The Hamiltonian then boils down to the well known Pariser-Parr-Pople Hamiltonian[14,15]:

$$H = -t \sum_{\langle ij, \rangle \sigma} \left\{ {c_{i\sigma}}^{\dagger} c_{j\sigma} + h.c. \right\} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} + \sum_{i>j} V_{ij}(n_i - z_i)(n_j - z_j) \tag{1.4}$$

The V_{ij}s are obtained by the Ohno parametrization[16]

$$V_{ij} = \frac{U}{\sqrt{1.0 + 0.6117 r_{ij}^2}}$$

where r_{ij} is the distance between 2 sites.

If the last term in Eq.1.4 is omitted, the Hamiltonian is the celebrated Hubbard Hamiltonian[17–19] , where electronic correlations is considered only at $r_{ij} = 0$.

$$H = -t \sum_{\langle ij, \rangle \sigma} \left\{ {c_{i\sigma}}^{\dagger} c_{j\sigma} + h.c. \right\} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} \tag{1.5}$$

However, the Eq.1.4 has complete long range Coulomb interactions, which is bridged between Hubbard U at r=0 and zero when $r \to \infty$, the truly ab-initio Hamiltonian. The Hamiltonians (Eq. 1.4 and 1.5) are too complicated to solve analytically. So there exist a number of computational methods to solve these Hamiltonians.

1.2 Computational Methods to Solve Many Body Hamiltonians

1.2.1 Exact Diagonalization

The Hamiltonian matrix is set up using the Fock basis states. The Hamiltonian matrix is diagonalized to obatain the eigenvalues and eigenvectors. There is no approximation involved in this method. It has been successfully applied to study properties of small low dimensional correlated systems[20–22].

Though it gives exact value of energies, large systems cannot be treated by this method as the Fock space grows exponentially with the number of sites. So there are some approximation methods which truncate the Fock basis set in such a way that the accuracy is maintained upto a good limit.

1.2.2 Variatinal Monte Carlo (VMC)

The Variational Monte Carlo is a stochastic method to calculate expectation values of Hamiltonians, developed by David M. Ceperley[23] in 1980. In this metod, a variational trial wave function is taken and the expectation values of the operators with respect to the wave function are obtained by Monte Carlo Integration, hence the name. It involves truncation of the basis set, as mentioned earlier. It can deal with large systems of any dimensions giving quite accurate values.

Variational Principle

If we have trial wave function $|\Psi(\{\alpha_i\})\rangle$, $\{\alpha_i\}$ being the set of parameters, then, according to the Variational Principle,

$$\frac{\langle\Psi(\alpha)|\hat{H}|\Psi(\alpha)\rangle}{\langle\Psi(\alpha)|\Psi(\alpha)\rangle} \geqslant E_0 \tag{1.6}$$

where E_0 is the exact ground state energy of the Hamiltonian.

The parameters $\{\alpha_i\}$ are called *Variatinal parameters*. They can be optimized to minimize the Variational energy expectation value so that it becomes as close to E_0 as possible.

The expectation value of an operator is given by

$$
\begin{aligned}
\langle \hat{A} \rangle &= \frac{\langle \Psi | \hat{A} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \\
&= \frac{\sum\limits_x \langle \Psi | x \rangle \langle x | \hat{A} | \Psi \rangle}{\sum\limits_x \langle \Psi | x \rangle \langle x | \Psi \rangle} \\
&= \frac{\sum\limits_x \frac{\langle x | \hat{A} | \Psi \rangle}{\langle x | \Psi \rangle} \left| \langle x | \Psi \rangle \right|^2}{\sum\limits_x \left| \langle x | \Psi \rangle \right|^2} \\
&= \sum_x w\left(x\right) \frac{\langle x | \hat{A} | \Psi \rangle}{\langle x | \Psi \rangle}
\end{aligned}
\tag{1.7}
$$

Where $w\left(x\right) \; = \; \dfrac{\left| \langle x | \Psi \rangle \right|^2}{\sum\limits_x \left| \langle x | \Psi \rangle \right|^2}$

The terms $\frac{\langle x | \hat{A} | \Psi \rangle}{\langle x | \Psi \rangle}$ are called the *local values* of the observables. Let us denote them by A_{loc}.

The $w\left(x\right)$ are the weight on the basis of which the local values of the observables A_{loc} are sampled using the Metropolis algorithm.

So the expectation value of the operator can be approximately written as

$$
\langle \hat{A} \rangle \; \approx \; \frac{1}{M} \sum_p \left(A_{loc}\right)_p \tag{1.8}
$$

where M is the total number of sampling steps and p is the index for the sampled out terms (p may have repititions, so total p is equal to M).
Let us make the notation $\langle x | \hat{A} | \Psi \rangle = A\psi\left(x\right)$ and $\langle x | \Psi \rangle = \psi\left(x\right)$
Then we can write

$$\langle\hat{A}\rangle \approx \frac{1}{M}\sum_{M}\frac{A\psi\left(x_p\right)}{\psi\left(x_p\right)} \tag{1.9}$$

The implementation of VMC for the Hubbard Hamiltonian has been given in detail in chapter 3.

1.2.3 Density Matrix Renormalization Group (DMRG) Method

DMRG method was developed by Steven R. White in 1992[24]. This is a very accurate method to calculate the eigenvalues and eigenvectors of strongly correlated lattice model Hamiltonians. This can treat large low dimensional systems (generally 1-dimensional and quasi 1-dimensional) which exact diagonalization cannot handle. In this method also, like QMC, there is truncation of the basis set, but the basis set here is different. Here, we start with a small system (generally 4 sites), and increase the number of sites by 2 in each iteration upto our desired size system or till the energy converges. The basis set is *renormalized* at every iteration.

Suppose we have a system and we divide it into 2 equal parts, which we call as subsystem and the environment[25]. If we wish to repesent the state of the system by the eigenvectors of the 2 smaller systems, then
the most general way to write the wavefunction of the total system $|\Psi\rangle$ as

$$|\Psi\rangle = \sum_{i,j} C_{ij}|\phi_i\rangle|\theta_j\rangle$$

which is written in terms of a mixed basis containing the direct product of eigenstates of both the systems or the subsystem and the environment.
Suppose we have an operator $\hat{A}$ which acts only on one of the basis sets, say, $|\phi_i\rangle$.

So, assuming $|\Psi\rangle$ to be a state of the total system, the *density matrix* is written as

$$\hat{\rho} = |\Psi\rangle\langle\Psi\rangle$$

So one of the elements of the density matrix is

$$\begin{aligned}\rho_{ij,kl} &= \langle\theta_l|\langle\phi_k|\Psi\rangle\langle\Psi|\phi_i\rangle|\theta_j\rangle \\ &= C^*_{kl}C_{ij}\end{aligned}$$

We ‘trace out’ 2 of the indices and get the *reduced density matrix*

$$\rho'_{ij} = \sum_{ll'} C^*_{il}C_{jl'}\delta_{ll'}$$

The expectation value of the operator $\hat{A}$ is

$$\langle\Psi|\hat{A}|\Psi\rangle = \sum_{ij} \rho'_{ij}\langle\phi_i|\hat{A}|\phi_j\rangle \tag{1.10}$$

In the above equation we see that, if we take $|\phi_i\rangle$ as the eigenvectors of the density matrix $|w_i\rangle$, then only the diagonal terms in this equation willl remain[25]. The expectation value of $\hat{A}$ in the density matrix eigenvector basis is

$$\langle\hat{A}\rangle = \sum_{i}^{N_C} w_i\langle w_i|\hat{A}|w_i\rangle$$

where N_C is the total number of states in Fock basis of the system

▶ Truncation of the basis set

The reduced density matrix has been brought into this picture because its eigenvectors represent the low energy of the whole system very well. We take only the first M highest eigenvalues and the corresponding eigenvectors. This is because lower the eigenvalues of the density matrix, lower is the probability density of that configuration.

So we have,

$$\langle\hat{A}_{approx}\rangle \approx \sum_{i}^{M} w_i\langle w_i|\hat{A}|w_i\rangle$$

This is extremely accurate. In fact, White and Huse(1993)[26] have calculated the ground state energy of a spin-1 isotropic Heisenberg chain accurately upto 12 decimal places.

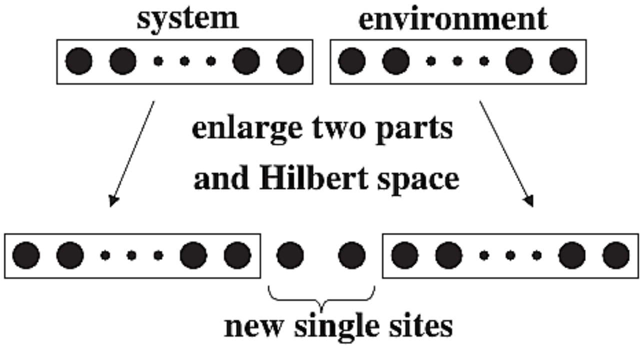
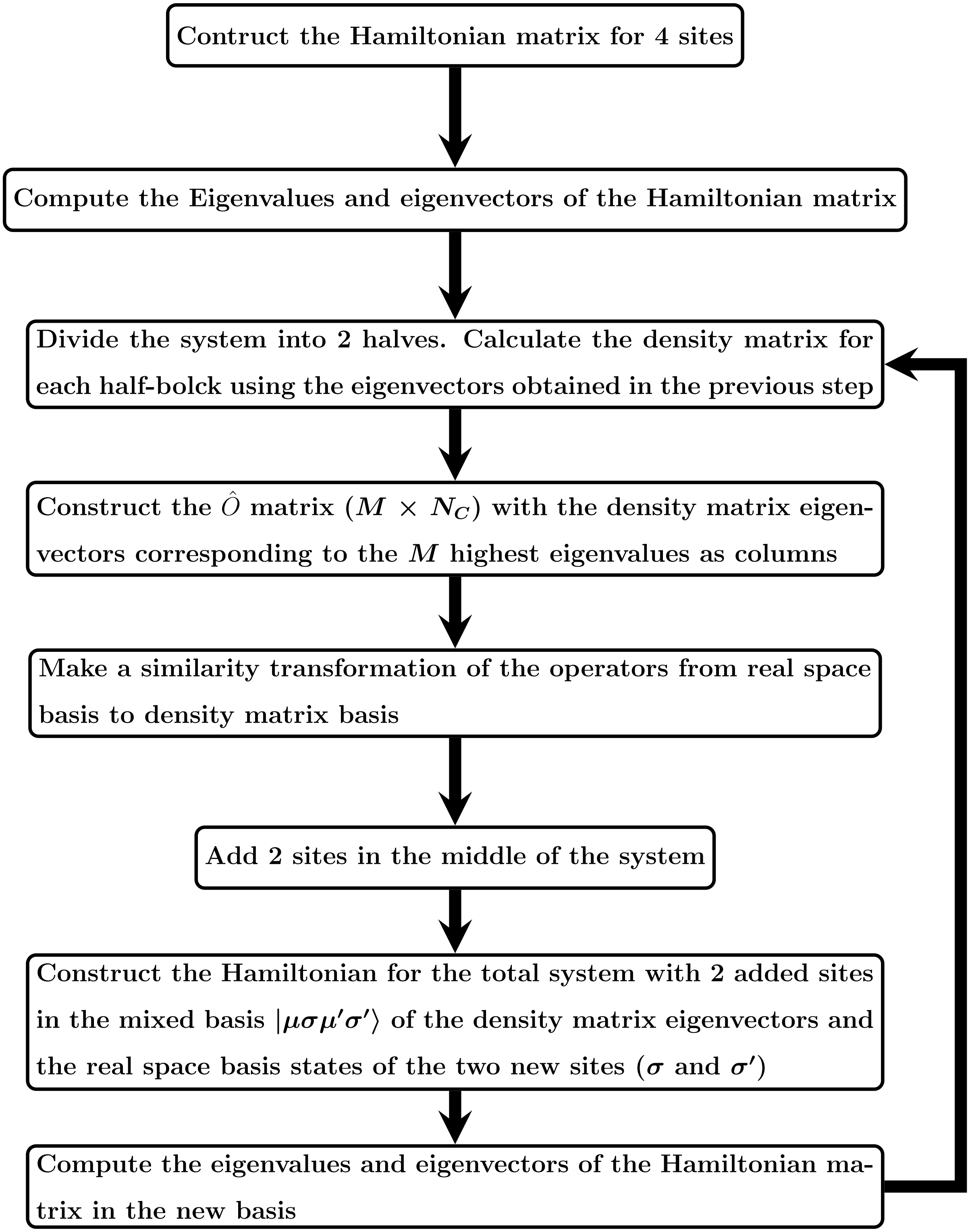


Figure 1.1: An iteration of DMRG method :the the full system is divided equally into a *system* and an *environment*.1 site is added to each of them, thus increasing the Hilbert space (the image is taken from J. Phys. Soc. Jpn. 70 8(2001)[27]

The algorithm for DMRG method is given in the following flowchart.



Contruct the Hamiltonian matrix for 4 sites

Compute the Eigenvalues and eigenvectors of the Hamiltonian matrix

Divide the system into 2 halves. Calculate the density matrix for each half-bolck using the eigenvectors obtained in the previous step

Construct the $\hat{O}$ matrix ($M \times N_C$) with the density matrix eigenvectors corresponding to the M highest eigenvalues as columns

Make a similarity transformation of the operators from real space basis to density matrix basis

Add 2 sites in the middle of the system

Construct the Hamiltonian for the total system with 2 added sites in the mixed basis $|\mu\sigma\mu'\sigma'\rangle$ of the density matrix eigenvectors and the real space basis states of the two new sites (σ and σ')

Compute the eigenvalues and eigenvectors of the Hamiltonian matrix in the new basis

We have used DMRG to calculate the non-linear magnetoelectric coefficients in correlated oligo acene systems. The results are given in Section 2.4.2.

- **Drawbacks of DMRG**

  DMRG can only deal with 1D and quasi 1D systems. It has not been reported to be very accurate for 2 or higher dimensional systems (although 2D algorithms have been constructed[28]).

1.2.4 Path Integral Renormalization Group(PIRG) Method

This method was developed by Imada's group in 2000[27] [29].

It has been named so because here, the Hubbard Stratonovich transformation has been used, which is used to write 2-body operators in terms of 1-body operators in quantum field theory.

In this method, a trial wave function is evolved in imaginary time, which after sufficiently large 'time' τ, give the ground state.

$$|\Psi_g\rangle \;=\; \lim_{\tau\to\infty} exp\{-\tau H\}|\Psi_t\rangle$$

Similar to Feynman's path integral formalism, the above projection is performed in n steps of $\Delta\tau$ and then this $\Delta\tau$ is considered to be sufficiently small and $n \to \infty$ so that,

$$|\Psi_g\rangle \;=\; \lim_{\Delta\tau\to 0}\left(\lim_{n\to\infty} exp\{-\Delta\tau H\}\right)|\Psi_t\rangle$$

But, at every iteration of $\Delta\tau$, new basis states are generated. This increases the number of basis sets. The basis set is thus truncated at each iteration and thus we get a *renormalized* basis set which is small enough to be handled computationally. At every iteration the the enegry is computed with the new basis set. If the energy is lower than the previous one, the basis set is accepted, otherwise it is rejected. This is how the basis set is renormalized at each iteration.

The implementation of the PIRG method has been given in detail in chapter 3.

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2

Magnetoelectric Effect in Quantum Many Body Systems

2.1 Introduction

There are systems in which a static magnetic field may induce an electric polarization and vice versa, i.e., a static electric field can induce a magnetization. Such systems are termed as Magnetoelectrics[1]. It was shown by Laudau and Lifshitz[2] that there exists a linear relationship between electric field and magnetization (or magnetic field and polarization) in some magnetic crystals in which time-reversal symmetry is broken. This phenomenon was predicted in Cr_2O_3 by Dzyaloshinskii[3] in 1959 and experimentally shown by Astrov[4] in the same year. Extensive reseach began when a class of materials called Multiferroics emerged out of experiments. These are materials in which both ferroelectricity and ferromagnetism can coexist. In recent years, large magnetoelectricity has been experimentally observed in many multiferroics like $BiFeO_3$, $TbMnO_3$ etc.

2.2 Magnetoelectricity : A Classical Approach

The Landau free energy of a system can be expressed as[1]

$$F(\vec{E},\vec{H}) = F_0 - \sum_i P_i^S E_i - \sum_i M_i^S H_i - \frac{1}{2}\sum_i\sum_j \epsilon_0\epsilon_{ij}E_iE_j - \frac{1}{2}\sum_i\sum_j \mu_0\mu_{ij}H_iH_j$$
$$- \sum_i\sum_j \alpha_{ij}E_iH_j - \frac{1}{2}\sum_i\sum_j\sum_k \beta_{ijk}E_iH_jH_k - \sum_i\sum_j\sum_k \gamma_{ijk}H_iE_jE_k - ... \tag{2.1}$$

where P^S and M^S are spontaneous polarization and magnetization respectively. The first derivatives of the free energy are the total Polarization and Magnetization, given by

$$P_i(\vec{E},\vec{H}) = -\frac{\partial F}{\partial E_i}\bigg|_{\vec{H}} = P_i^S + \sum_j \epsilon_0\epsilon_{ij}E_j + \sum_j \alpha_{ij}H_j + \frac{1}{2}\sum_j\sum_k \beta_{ijk}H_jH_k$$
$$+ \sum_j\sum_k \gamma_{ijk}H_jE_k - ... \tag{2.2}$$

and

$$M_i(\vec{E},\vec{H}) = -\frac{\partial F}{\partial H_i}\bigg|_{\vec{E}} = M_i^S + \sum_j \mu_0\mu_{ij}H_j + \sum_j \alpha_{ij}E_j + \frac{1}{2}\sum_j\sum_k \beta_{ijk}E_jH_k$$
$$+ \sum_j\sum_k \gamma_{ijk}E_jE_k - ... \tag{2.3}$$

Time reversal symmetry breaking for linear magnetoelectrics

For *linear* magnetoelectrics, the polarization $\vec{P} = \bar{\bar{\alpha}}\vec{H}$.

Suppose the system has time reversal symmetry. We apply the *time reversal* operator $\boldsymbol{R}$ on both sides. $\boldsymbol{R}$ changes $\vec{H}$ to -$\vec{H}$.

So,

$$\boldsymbol{R}\{\vec{P}=\bar{\bar{\alpha}}\vec{H}\} \implies \vec{P}=\bar{\bar{\alpha}}(-\vec{H}) \quad \equiv \quad \vec{P}=\bar{\bar{\alpha}}(\vec{H})$$

So $\bar{\bar{\alpha}}$ should be **zero**. Hence there should be broken time reversal symmetry.

- ▶ The *spatial inversion symmetry* should also be broken for linear magnetoelectricity. Suppose, we operate by the inversion symmetry operator $\boldsymbol{I}$, $\vec{P}$ transforms to $-\vec{P}$ with all others unchanged, resulting in $\bar{\bar{\alpha}}$ to be zero.
- ▶ For nonlinear magnetoelectrics, this is not a necessary condition.

2.2.1 Magnetization by External Electric Field

Magnetoelectricity has been experimentally reported mostly in materials which are antiferromagnetic in nature. The structure of antiferromagnets like Cr_2O_3 are such that there is a magnetic cation (Cr^{3+}) and a non-magnetic anion (O^{2-}), which remain in pairs. When there is no electric field, the net polarization and magnetization are zero. Upon application of an electric field parallel to the direction of the 'chain' of magnetic ions (as shown in figure 1.2), the cations and the anions move closer. This affects the orbital overlap of the electrons, thus changing their orbital motion and hence their net magnetic moment[5]. This produces a non-zero magnetization in the crystal i.e. we get a non-zero $\vec{M}=\alpha\vec{E}$

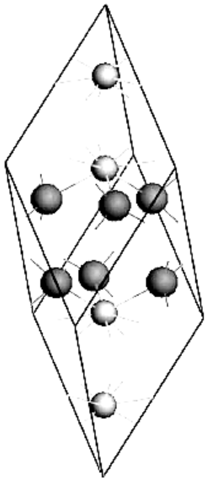


Figure 2.1: Cr_2O_3 unit cell structure[6]. Black : O^{2-}, white atoms: Cr^{3+}

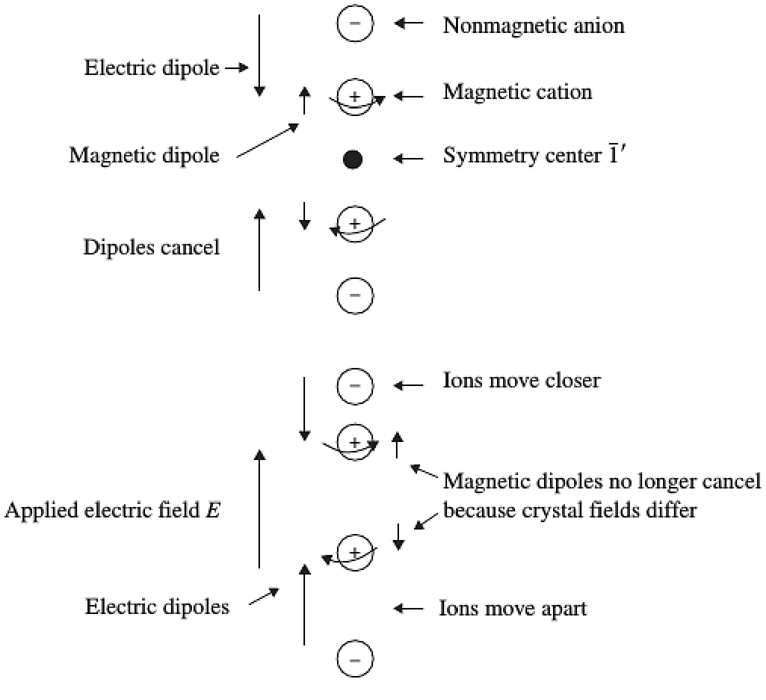


Figure 2.2: One dimensional description of how an external electric field produces a non-zero magnetization(taken from pg. 142 of the book *Properties of Materials Anisotropy, Symmetry, Strucutre*[7])

2.2.2 Polarization by External Magnetic Field

Spiral Magnets

Neutron Diffraction studies suggest that multiferroic materials such as $TbMnO_3$and $Ni_3V_2O_8$ have a spiral magnetic ordered phase. That is, the spin vectors are aligned in such a way that their directions vary periodically along some arbitrary direction forming a spiral pattern. These type of systems have spin-spin interactions of the type $\vec{\boldsymbol{D}}.\vec{\boldsymbol{S}}_{\boldsymbol{i}} \times \vec{\boldsymbol{S}}_{\boldsymbol{i}}$ (Dzyaloshinskii-Moriya interactions[8,9]) or $\vec{\boldsymbol{D}} \times \vec{\boldsymbol{S}}_{\boldsymbol{1}} \times \vec{\boldsymbol{S}}_{\boldsymbol{2}}$, which gives rise to both linear and non-linear magnetoelectric coefficients[10–12]

2.3 Magnetoelectricity : A quantum mechanical approach

2.3.1 Calculation of ME coefficients from Many Body Electronic Hamiltonians (Our Approach)

The ME coefficient study in the literature has been limited to mostly atomic systems and its formalism also is developed for atomic (one body) systems only. Here, however, we consider a low dimensional strongly correlated conjugated carbon systems and describe these by considering the PPP Hamiltonian.

$$H = -t \sum_{\langle ij,\rangle \sigma} \left\{ {c_{i\sigma}}^{\dagger} c_{j\sigma} + h.c. \right\} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} + \sum_{i>j} V_{ij} (n_i - z_i)(n_j - z_j) \quad (2.4)$$

where $n_{i\sigma} = c^{\dagger}_{i\sigma} c_{i\sigma}$ is the number operator for site i and spin σ (↑ or ↓)

and $n_i = n_{i\uparrow} + n_{i\downarrow}$

V_{ij} is the long range coulomb interaction[13]

$V_{ij} = \frac{U}{\sqrt{1.0+0.6117 r_{ij}^2}}$ where r_{ij} is the distance between 2 sites in Å

Some of the results are given in section 2.4 From Eqn.2.1, the 2$^{\text{nd}}$ order non-linear ME coefficient tensors γ_{ijk} and β_{ijk} can be written as

$$\gamma_{ijk} = \frac{\partial^3 F}{\partial E_i \partial E_j \partial H_k}$$

involving **2 electric fields and 1 magnetic field**, and

$$\beta_{ijk} = \frac{\partial^3 F}{\partial E_i \partial H_j \partial H_k}$$

involving **2 magnetic fields and 1 electric field** .

which are actually the 3$^{\text{rd}}$ order derivatives of energy with respect to the fields. To calculate them computationally, we have to *discretize* these terms.

2.3.1.1 Explicit Electric and Magnetic field terms in the Hamiltonian

We include the electric field terms explicitly in the Hamiltonian :

$$\sum_i n_i \vec{E}.\vec{r_i} \qquad \text{where } n_i = n_{i\uparrow} + n_{i\downarrow}$$

i.e., the electric field interacts with the total charge at each site thus having a potential energy term $(n_i\vec{E}).\vec{r_i}$

The Magnetic field term is introduced explicitly as

$$\sum_i \vec{B}.\vec{S_i}$$

where irrespective of the dimensions of the system, the spin has 3 degrees of freedom. S_z is mostly used in analysis as it is diagonal and thus easy to handle. But have no idea about the values of S_x and S_y. We cannot determine all 3 at the same time as they do not commute. Hence for many body systems, we will always have to consider all the 3 components of $\vec{B}.\vec{S_i}$.

2.3.1.2 Calculation of γ_{ijk} involving 2 Electric field and 1 Magnetic field terms

We include 2 electric and 1 magnetic field terms in the Hamiltonian :

$$\sum_i n_i \vec{E}_1.\vec{r}_i \ , \quad \sum_i n_i \vec{E}_2.\vec{r}_i \quad \text{and} \quad \sum_i \vec{B}.\vec{S}_i$$

Let us calculate γ_{ijk} first. It is easy to see that

$$\begin{aligned}\sum_{ijk} \gamma_{ijk} E_i E_j H_k = F(\vec{E}_1, \vec{E}_2, \vec{H}_1) - F(-\vec{E}_1, \vec{E}_2, \vec{H}_1) - F(\vec{E}_1, -\vec{E}_2, \vec{H}_1) \\ - F(\vec{E}_1, \vec{E}_2, -\vec{H}_1) + F(-\vec{E}_1, -\vec{E}_2, \vec{H}_1) + F(\vec{E}_1, -\vec{E}_2, -\vec{H}_1) \\ + F(-\vec{E}_1, \vec{E}_2, -\vec{H}_1) + F(-\vec{E}_1, -\vec{E}_2, -\vec{H}_1) \quad (2.5)\end{aligned}$$

We assume that $|E_i E_j H_k| = constant = C$ for all i,j,k

We define $\sum_{ijk} \gamma_{ijk} = \gamma_{eff}$, then ,

γ_{eff} can be written in a discrete form

$$\begin{aligned}\gamma_{eff} = \frac{1}{8C} \Bigg[F_{tot}(\vec{E}_1, \vec{E}_2, \vec{H}_1) - F_{tot}(-\vec{E}_1, \vec{E}_2, \vec{H}_1) - F_{tot}(\vec{E}_1, -\vec{E}_2, \vec{H}_1) \\ - F_{tot}(\vec{E}_1, \vec{E}_2, -\vec{H}_1) + F_{tot}(-\vec{E}_1, -\vec{E}_2, \vec{H}_1) + F_{tot}(\vec{E}_1, -\vec{E}_2, -\vec{H}_1) \\ + F_{tot}(-\vec{E}_1, \vec{E}_2, -\vec{H}_1) + F_{tot}(-\vec{E}_1, -\vec{E}_2, -\vec{H}_1) \Bigg] \quad (2.6)\end{aligned}$$

Where, for instance $F_{tot}(\vec{E}_1, \vec{E}_2, \vec{H}_1)$ is the sum of all the energies obtained for all positive componets of the electric and magnetic field vectors. That is, $F_{tot}(\vec{E}_1, \vec{E}_2, \vec{H}_1) = \sum_{ijk} F(E_{1i}, E_{2j}, H_{1k})$, i, j, k being the components of the electric and magnetic field vectors. This sum will run over 27 terms for a 3-dimensional system.

Similar is the case for the other 7 F_{tot} terms.

2.3.1.3 Calculation of β_{ijk} involving 2 Magnetic field and 1 Electric field terms

Similarly, as in the previous case, here $|E_i H_j H_k| = constant = C'$ for all i,j,k

We define $\sum_{ijk} \beta_{ijk} = \beta_{eff}$. So, β_{eff} can be discretized as

$$\begin{aligned}\beta_{eff} = \frac{1}{8C'}\Big[& F_{tot}(\vec{E}_1, \vec{H}_1, \vec{H}_2) - F_{tot}(-\vec{E}_1, \vec{H}_1, \vec{H}_2) - F_{tot}(\vec{E}_1, -\vec{H}_1, \vec{H}_2) \\ & - F_{tot}(\vec{E}_1, \vec{H}_1, -\vec{H}_2) + F_{tot}(-\vec{E}_1, -\vec{H}_1, \vec{H}_2) + F_{tot}(\vec{E}_1, -\vec{H}_1, -\vec{H}_2) \\ & + F_{tot}(-\vec{E}_1, \vec{H}_1, -\vec{H}_2) + F_{tot}(-\vec{E}_1, -\vec{H}_1, -\vec{H}_2)\Big]\end{aligned} \tag{2.7}$$

Here also each F_{tot} will have 27 terms, if all the field vectors have non-zero components in all 3 directions.

2.3.2 Quantum mechanical Origin of ME Coefficients from Electronic motion only

From eq. 2.6, it is clear that the discretized form of ME coeffecient γ_{eff} consists of terms obtained by reversing the direction of electric and mangnetic fields.
, i.e., for instance,

$$F_{tot}\left(\vec{E}_1, \vec{H}_1, \vec{H}_2\right) \neq F_{tot}\left(-\vec{E}_1, \vec{H}_1, \vec{H}_2\right) \tag{2.8}$$

To obtain non-zero ME coeffecients, it is necessary that at least one term in Eq. 2.7 should obey Eq. 2.8
In fact, we argue that, one particle physics will not be able to give ME coefficients when only electronic motion is considered. Here is how is is explained. Suppose

we have a 'free' particle of charge q. We add an electric field $\boldsymbol{q\vec{E}.\vec{r}}$. If we try to find the 1st order perturbation correction of energy it is zero.

$$\int_{-\infty}^{+\infty} e^{-i\vec{k}.\vec{r}} x e^{i\vec{k}.\vec{r}} d^3r \;=\; 0$$

So the energy is the same for both $+E$ and $-E$.

Now, turning to many electron systems, if we consider only tight binding terms, the electrons are completely delocalized, so 1st order energy change due to electric field (which, in this case, is proportional to $\langle \hat{n}_i r_i \rangle$, $\hat{n}_i$ being the number operator) is zero.

As soon as we introduce the Hubbard term (or other terms which localize the electrons), $\langle \hat{n}_i \rangle$ becomes non-zero.

In fact, for large U, $\langle x_i \rangle$ is 1 for all sites i. Hence, we get a linear energy correction term, and so the energy will differ when the electric field direction is reversed.

This gives the nonzero ME coefficients.

In case of magnetic field, since $\hat{S}_z$ commutes with the Hamiltonian, the terms $H_x\hat{S}_x$ and $H_y\hat{S}_y$ changes the S_z^{total} value but they have linear contribution (and they appear in ± pairs in the eigenvalues) to the energies, which will be shown in the follwing section.

2.4 Results and Discussions

2.4.1 Behaviour of Many body systems in presence of $\vec{E}$ and $\vec{H}$ fields : A study with a simple 2-site model

Let us consider a system of of 2 sites and 2 electrons and total $S_z = 0$ The basis set then consists of 4 configurations:

$$\underline{\uparrow\;\downarrow}\qquad \underline{\downarrow\;\uparrow}\qquad \underline{0\quad\uparrow\downarrow}\qquad \underline{\uparrow\downarrow\quad 0}$$

The last 2 configurations have a Hubbard U term.

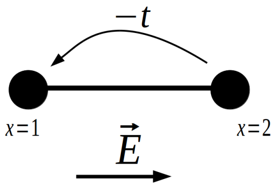


Figure 2.3

The Hubbard Hamiltionian for this system can be written as

$$H = -t\sum_{\sigma=\uparrow,\downarrow}\left\{{c_{1\sigma}}^{\dagger}c_{2\sigma} + {c_{2\sigma}}^{\dagger}c_{1\sigma}\right\} + U\left\{n_{1\uparrow}n_{1\downarrow} + n_{2\uparrow}n_{2\downarrow}\right\}$$

The matrix of the Hamiltonian constructed from the above basis states is

$$\begin{bmatrix} 0 & 0 & -t & -t \\ 0 & 0 & -t & -t \\ -t & -t & U & 0 \\ -t & -t & 0 & U \end{bmatrix}$$

▶ Linear Electric Field term in the Hamiltonian generates Non-linear terms in the Energy

We define a coordinate system with the two atoms at two points $x = 1$ and $x = 2$ (as in fig. 2.3) Now we put an electric field term parallel to the line joining the 2 atoms.

So there will be an extra term in the Hamiltonian : $n_1 E x_1 + n_2 E x_2$

Putting $t = 1$ (So that the analytical expression looks simpler) The resultant matrix will be

$$\begin{bmatrix} 3E & 0 & -1 & -1 \\ 0 & 3E & -1 & -1 \\ -1 & -1 & 2E+U & 0 \\ -1 & -1 & 0 & 4E+U \end{bmatrix}$$

The eigenvalues of this matrix (solved partly in *Mathematica*) are :

$$\lambda_1 = 3E$$

$$\lambda_2 = (3E+\frac{2}{3}U)-2\sqrt{\frac{12+3E^2+U^2}{9}}\cos\left\{\frac{1}{3}\arccos\left(\frac{U(-18+9E^2-U^2)}{\sqrt{3}(12+3E^2+U^2)^{\frac{3}{2}}}\right)\right\}$$

$$= (3E+\tfrac{2}{3}U) - \boldsymbol{g\,(E^2, U)}$$

$$\lambda_3 = (3E+\frac{2}{3}U) - 2\sqrt{\frac{12+3E^2+U^2}{9}}\cos\left\{\frac{1}{3}\arccos\left(\frac{U(-18+9E^2-U^2)}{\sqrt{3}(12+3E^2+U^2)^{\frac{3}{2}}}\right) - \frac{2\pi}{3}\right\}$$

$$= (3E+\tfrac{2}{3}U) - \boldsymbol{g'\,(E^2, U)}$$

$$\lambda_4 = (3E + \frac{2}{3}U) - 2\sqrt{\frac{12+3E^2+U^2}{9}}\cos\left\{\frac{1}{3}\arccos\left(\frac{U(-18+9E^2-U^2)}{\sqrt{3}(12+3E^2+U^2)^{\frac{3}{2}}}\right) - \frac{4\pi}{3}\right\}$$

$= (3E + \frac{2}{3}U) - \boldsymbol{g''(E^2, U)}$

These functions $\boldsymbol{g}$, $\boldsymbol{g'}$, and $\boldsymbol{g''}$ are functions of E^2.

So, clearly,the expressions have a linear E term which will change when E is changed to $-E$.

We see that only a electric linear electric field term in the generates non-linear terms in the energy eigenvalues.

► Linear Magnetic Field Term has only Linear Contribution to the Energy

Now we put a magnetic field $\vec{H}$ in the system.

Though the system is 1-dimensional, the spin $\vec{s}$ has components along all 3 directions.

For this, there will be another term in the Hamiltionian : $H_xS_x + H_yS_y + H_zS_z$.

As total $S_z = 0$, there will be no contribution from H_z.

The other 2 components can be written as $S_x = \frac{S_+ + S_-}{2}$ and $S_y = \frac{S_+ - S_-}{2i}$, where S_+ and S_- are the spin raising and lowering opertors respectively.

Now,

$S_+|\underline{0 \;\; \uparrow\downarrow}\rangle = (S_{1+} + S_{2+})\,|\underline{0 \;\; \uparrow\downarrow}\rangle = 0$ and also

$S_+|\underline{\uparrow\!\downarrow\ \ 0}\,\rangle \; = \; 0$

Simlarly, $S_-|\underline{\uparrow\!\downarrow\ \ 0}\,\rangle \; = \; 0$ and $S_-|\underline{\uparrow\!\downarrow\ \ 0}\,\rangle \; = \; 0$

$S+$ and S_- acting on $|\underline{\uparrow\ \downarrow}\rangle$ and $|\underline{\downarrow\ \uparrow}\rangle$ will generate 2 new states: $|\underline{\uparrow\ \uparrow}\rangle$ and $|\underline{\downarrow\ \downarrow}\rangle$ which are not in the basis set of the 4 states.
Hence the magnetic field will have no terms in the matrix. Thus, as we found, if we consider that total spin is *conserved* ($total\,\mathrm{S}_z = 0$ in the above example), there is non effect of the magnetic field.

Now we increase the basis set by adding the above mentioned 2 new states. So the states are :

$$\underline{\uparrow\ \uparrow} \qquad \underline{\uparrow\ \downarrow} \qquad \underline{\downarrow\ \uparrow} \qquad \underline{\mathbf{0}\ \ \uparrow\!\downarrow} \qquad \underline{\uparrow\!\downarrow\ \ \mathbf{0}} \qquad \underline{\downarrow\ \downarrow}$$

In this basis set, the total S_z is not conserved

In this case, the matrix will be 6×6 one

$$\begin{bmatrix}
3E + H_z & \frac{1}{2}(H_x + iH_y) & \frac{1}{2}(H_x + iH_y) & 0 & 0 & 0 \\
\frac{1}{2}(H_x - iH_y) & 3E & 0 & -1 & -1 & \frac{1}{2}(H_x + iH_y) \\
\frac{1}{2}(H_x - iH_y) & 0 & 3E & -1 & -1 & \frac{1}{2}(H_x + iH_y) \\
0 & -1 & -1 & 2E + U & 0 & 0 \\
0 & -1 & -1 & 0 & 4E + U & 0 \\
0 & \frac{1}{2}(H_x - iH_y) & \frac{1}{2}(H_x - iH_y) & 0 & 0 & 3E - H_z
\end{bmatrix}$$

This is a very complicated matrix to handle analytically.
To obtain the eigenvalues, we need to solve a 6^{th} degree polynomial equation which, in general, have no algeraic form.

First, we notice that 2 of the basis states , $\underline{0\quad\uparrow\downarrow}$ and $\underline{\uparrow\downarrow\quad 0}$ have no effect when the magnetic field is turned on. So for the ME coefficient, we consider the 4×4 matrix formed by the rest 4 basis states.

$$M = \begin{pmatrix} 3e + H_z & \frac{1}{2}\left(H_x + iH_y\right) & \frac{1}{2}\left(H_x + iH_y\right) & 0 \\ \frac{1}{2}\left(H_x - iH_y\right) & 3e & 0 & \frac{1}{2}\left(H_x + iH_y\right) \\ \frac{1}{2}\left(H_x - iH_y\right) & 0 & 3e & \frac{1}{2}\left(H_x + iH_y\right) \\ 0 & \frac{1}{2}\left(H_x - iH_y\right) & \frac{1}{2}\left(H_x - iH_y\right) & 3e - H_z \end{pmatrix} \tag{2.9}$$

Algebraic expression for γ_{eff} and β_{eff} for 2 sites

The terms for the electric and magnetic field present here are $\vec{E_1} = \{E_{1x}\}$, $\vec{E_2} = \{E_{2x}\}$ and $\vec{H_1} = \{H_{1x}, H_{1y}, H_{1z}\}$

So, to calculate γ_{eff} we calculate the energies each time with the following field terms:

1. $E_{1x},\ E_{2x}\ H_{1x}$
2. $E_{1x},\ E_{2x}\ H_{1y}$
3. $E_{1x},\ E_{2x}\ H_{1y}$

The eigenvalues in the 1st case are:

$3(E_{1x} + E_{2x}),\ 3(E_{1x} + E_{2x}),\ 3(E_{1x} + E_{2x}) + H_{1x},$ and $3(E_{1x} + E_{2x}) - H_{1x}$

The eigenvalues in the 2nd case are:

$$3(E_{1x}+E_{2x}),\ \ 3(E_{1x}+E_{2x}),\ \ 3(E_{1x}+E_{2x})+H_{1y},\ \text{ and }\ 3(E_{1x}+E_{2x})-H_{1y}$$

The eigenvalues in the 3rd case are:

$$3(E_{1x}+E_{2x}),\ \ 3(E_{1x}+E_{2x}),\ \ 3(E_{1x}+E_{2x})+H_{1z},\ \text{ and }\ 3(E_{1x}+E_{2x})-H_{1z}$$

In all the cases, the eigenvalues have the same form.

If all H_{1x}, H_{1z} and H_{1z} are positive, the ground state would be $(3(E_{1x}+E_{2x})-H_{1x})$, or $(3(E_{1x}+E_{2x})-H_{1y})$ or $(3(E_{1x}+E_{2x})-H_{1z})$

Clearly, $(3(E_{1x}+E_{2x})\pm H_{1i})$ $(i=1,2,3)$ come in pairs. So, if the $H_{1i} \implies -H_{1i}$, then the ground state will be $\{3(E_{1x}+E_{2x})+(-H_{1i})\}$, i.e. $\{3(E_{1x}+E_{2x})+H_{1i}\}$ That is, the ground state does not change.

The 2nd order ME coefficient will not have **no** any non-zero term from the magnetic field.

In this case $\gamma_{eff} = \dfrac{15(E_{1x}+E_{2x})}{4C}, (C = constant)$

In fact, the eigenvalues of the matrix M(eqn. 2.9) with $E = (E_{1x}+E_{2x})$ and $\vec{H} = \vec{H}_1$ are

$$\lambda_1 = 3(E_{1x}+E_{2x}) \qquad \lambda_2 = 3(E_{1x}+E_{2x})$$
$$\lambda_3 = 3(E_{1x}+E_{2x})-\sqrt{H_x^2+H_y^2+H_z^2} \qquad \lambda_4 = 3(E_{1x}+E_{2x})+\sqrt{H_x^2+H_y^2+H_z^2}$$

The ground state is clearly λ_3.

Since there is no cross terms (E_iH_j, $E_iE_jH_k$, $E_iH_jH_k$ etc. terms), the ME coefficients

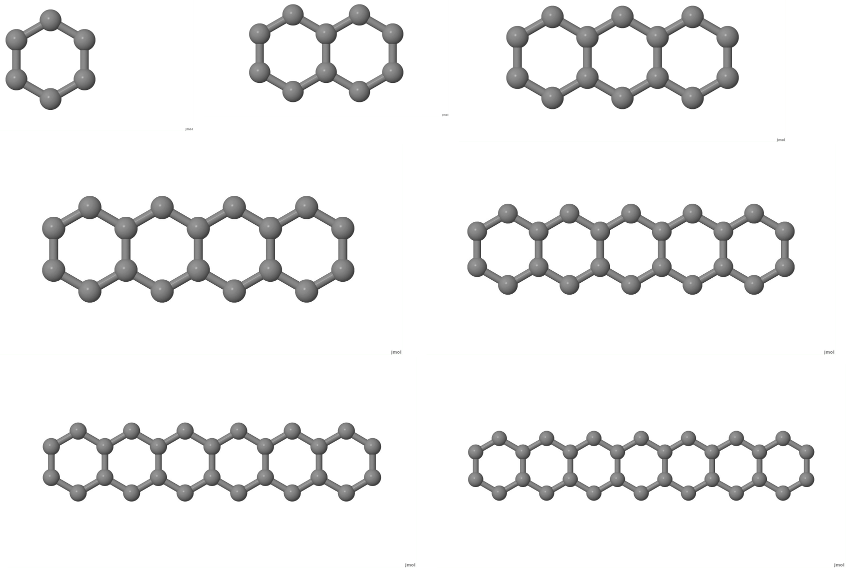
$$\gamma_{ijk} = \frac{\partial^3 F}{\partial E_i \partial E_j \partial H_k} = 0 \text{ and}$$

$$\beta_{ijk} = \frac{\partial^3 F}{\partial E_i \partial E_j \partial H_k} = 0$$

2.4.2 Second order ME coefficients in acenes : A DMRG Study

The 2^{nd} order nonlinear ME coeffecients γ_{eff} and β_{eff} have been calculated from the PPP Hamiltionian with electric and magnetic field terms explicitly added, as mentioned in 2.3.1.1.

The systems which we targetted first, are two leg ladder systems with alternate rung interaction missing (there are real conjugated carbon systems with this structure, named as oligo acenes). These are *low dimensional* systems for which the Hamiltonian can be solved with great accuracy with the DMRG method (Chapter 1).



These acenes are correlated systems. The ground state of each of these systems is a singlet. (cite the reference). In fact, we have calculated the spin density of these systems upto 15 rings (62 atoms).

2.4.2.1 Calculations for 2 electric and 1 magnetic fields

The electric field terms only along the plane of the acene(taken as the x-y plane) molecule will have non-zero contributions (the component along z axis will have $\vec{E_z}.\vec{r_i} = 0$)

On the other hand, since the spins $\vec{S_i}$ are 3-dimensional, hence there will be contributions from all 3 directions.

So, $\vec{E_1} = \{E_{1x}, E_{1y}\}$, $\vec{E_2} = \{E_{2x}, E_{2y}\}$ and $\vec{H_1} = \{H_{1x}, H_{1y}, H_{1z}\}$

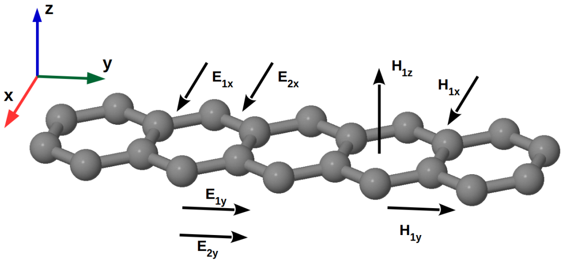


Figure 2.4: Direction of applied fields

So each F_{tot} will consist of 12 terms (4 electric field and 3 magnetic field).
Hence Eq.2.6 will have **96** energy terms. Each of these terms are obtained by solving the Hamiltonian 96 times with their directions changed (i.e. the signs of the components reversed).
For example, a few initial conditions are given below

$\vec{E_1}$:	**0.100**	0.000	0.000	$\vec{E_1}$:	**-0.100**	0.000	0.000	$\vec{E_1}$:	0.000	**-0.001**	0.000
$\vec{E_2}$:	**0.100**	0.000	0.000	$\vec{E_2}$:	0.000	**0.100**	0.000	$\vec{E_2}$:	**-0.100**	0.000	0.000
$\vec{H_1}$:	0.000	0.000	**0.001**	$\vec{H_1}$:	0.000	0.000	**-0.001**	$\vec{H_1}$:	0.000	**-0.001**	0.000

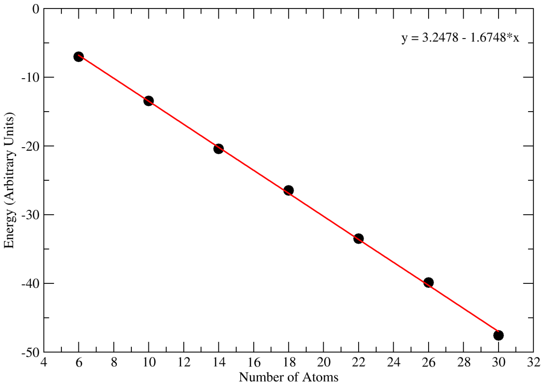


Figure 2.5: Variation of ground state with the number of atoms

Thus there are 96 such initial inputs.

In all the calculations we have assumed that $|E_iE_jH_k|$ to be constant .

The hopping parameter t, Hubbard term U and the distance between atoms, r_{ij} are taken as 2.4 eV, 11.26 eV and 1.4 Å respectively (These are the parameters for conjugated carbon systems, as reported in literature).

The DMRG calculations show that the groud state energies vary linearly with the numer of atoms (or the number of rings). For instance, here is the variation of energy vs the number of atoms for following field values : $E_{1x} = -0.1,\ \ E_{2x} = 0.1,\ \ H_{1z} = 0.001$

The variation of magnetoelectric coefficients γ_{eff} vs no. of atoms is given in the figure below.

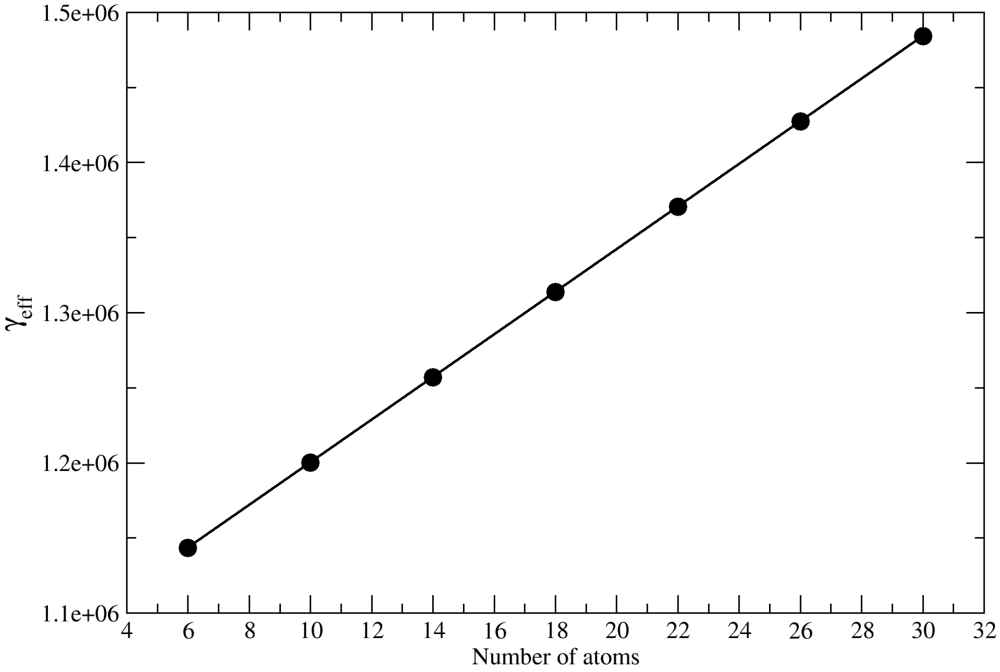


Figure 2.6: Variation of γ_{eff} with the number of atoms

And below are individual contributions obtained by switching the signs of the fields

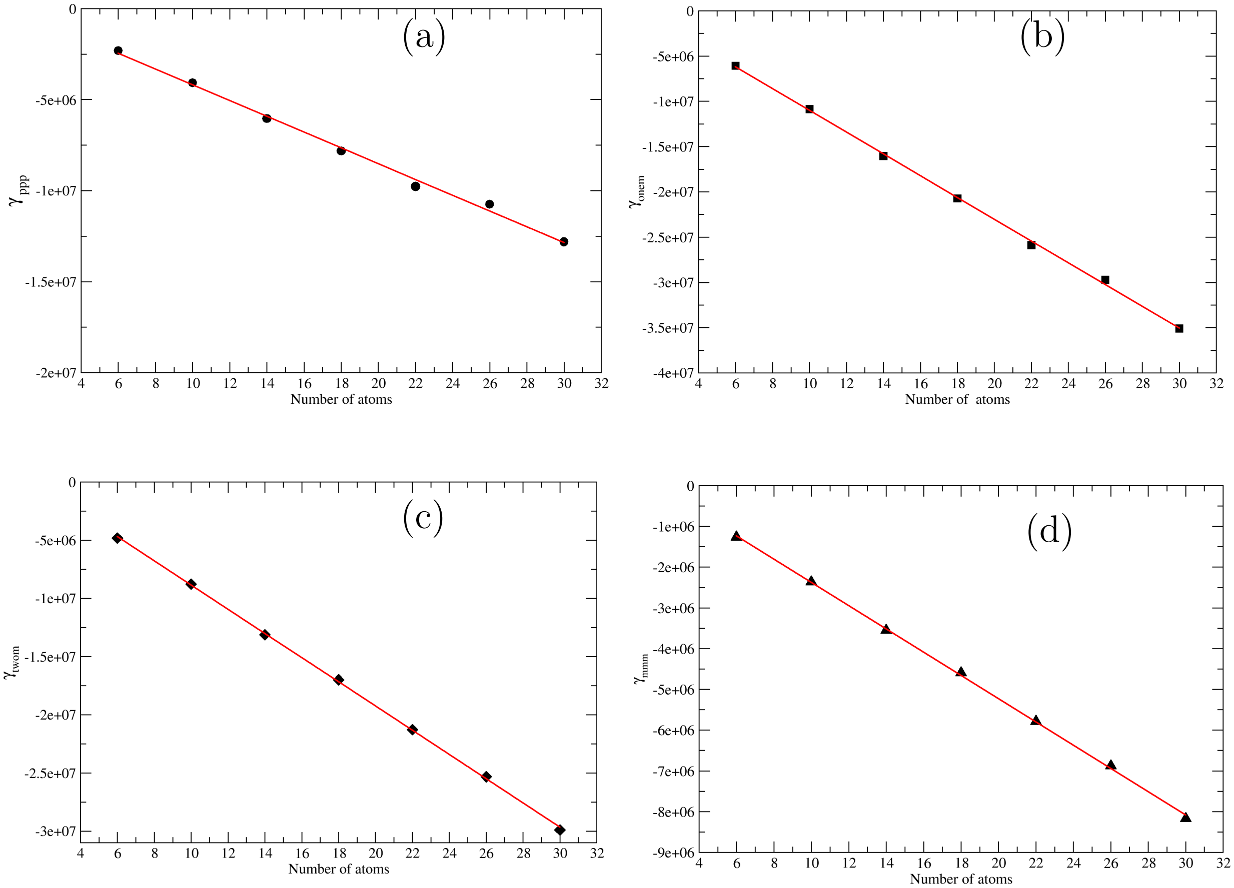


Figure 2.7: Contributions to the ME coefficient β_{eff} in case of (a)all positive(b) 2 negative 1 positive (c)2 negative and 1 positive (d) all negative field terms(along with linear fit)

Since the increase in energies vs the number of atoms is linear, it is obvious that the ME coefficients, being a linear function of the energies will also vary linearly with the number of atoms.

2.4.2.2 Calculations for 2 magnetic and 1 electric fields

In this case, the fields are

$\vec{E_1} = \{E_{1x}, E_{1y}\}$, $\vec{H_1} = \{H_{1x}, H_{1y}, H_{1z}\}$ and $\vec{H_2} = \{H_{2x}, H_{2y}, H_{2z}\}$

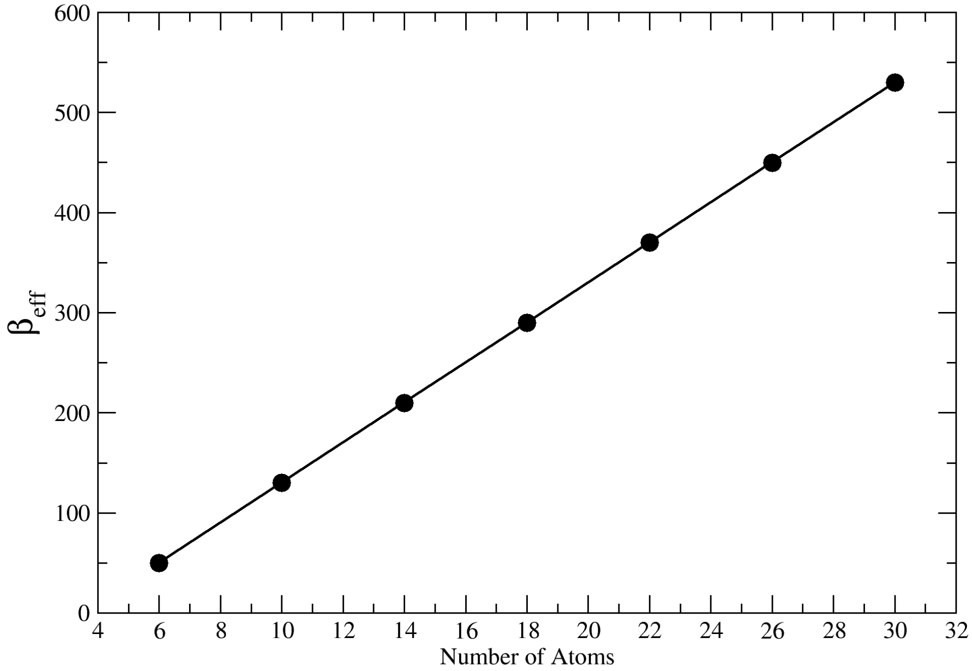


Figure 2.8: Variation of β_{eff} with the number of atoms

And these are individual contributions obtained by switching the signs of the fields

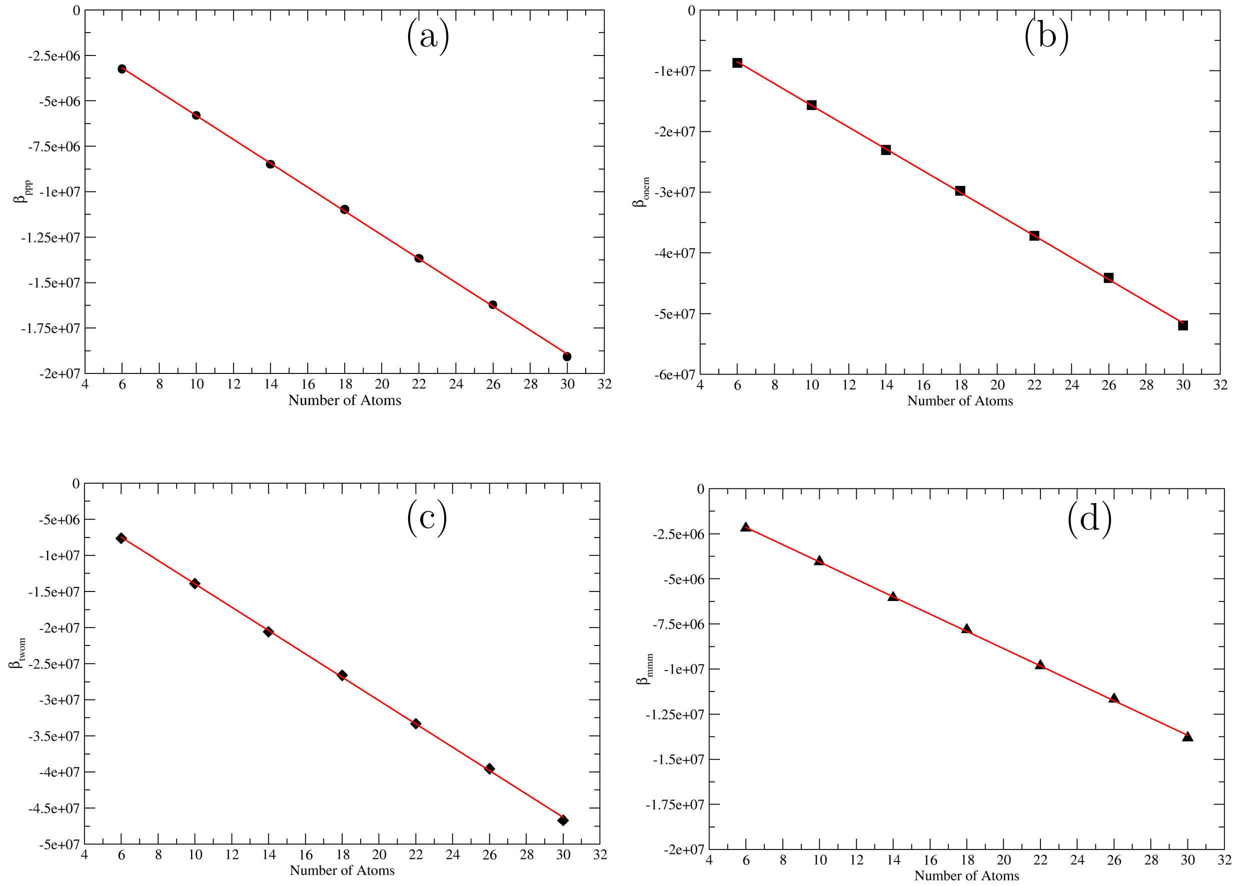


Figure 2.9: Contributions to the ME coefficient β_{eff} in case of (a)all positive(b) 2 negative 1 positive (c)2 negative and 1 positive (d) all negative field terms(along with linear fit)

In this case also, the variations are linear, as expected. Although the indiviadual term contributions are large, they result in a small ME coefficient, as many of the terms get cancelled out. This is because there are 2 magnetic field terms, which affect the energies much lesser compared to the previous case with two electric field terms. The coefficient computed for two magnetic and one electric field has lower magnitude in comparison to the coeffecients which are obtained with two electric and one magnetic field term. This is because as we have seen in case of 2 sites case, the magnetic field terms do not contribute at all. Since in these systems, there is no spin-flip or spin fluctuation terms, the magnetic field term can not change the energy of the system.

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3

Implementation of Variational Monte Carlo and Path Integral Renormalization Group Methods

In this chapter, we discuss two computational methods for quantum many body problem, which we have implemented for the Hubbard Hamiltonian. We will discuss below the details on each method and how we have implemented each of the methods in computational code. We have checked the methods by calculating energies for some small systems and verified the accuracy by calculating the same from exact diagonalization method.

3.1 Variational Monte Carlo Method for the Hubbard Hamiltonian

The Hubbard Hamiltonian[1] for a lattice is written as

$$H = -t \sum_{\langle ij, \rangle \sigma} \left\{ {c_{i\sigma}}^{\dagger} c_{j\sigma} + h.c. \right\} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} \tag{3.1}$$

The Variational Monte Carlo[2,3], as introduced in Chapter 1, is a very powerful method to treat large systems with or without correlation. We take a Variational trial wave function. It uses Monte Carlo sampling to calculate the expectation values of the energy and other operators. In Eq. 1.9, we see that the expectation value of an operator is given by

$$\begin{aligned} \langle \hat{A} \rangle &= \frac{\langle \Psi | \hat{A} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \\ &\approx \frac{1}{M} \sum_{M} \frac{A\psi\left(x_p\right)}{\psi\left(x_p\right)} \end{aligned} \tag{3.2}$$

where $A\psi\left(x\right) = \langle x | \hat{A} | \Psi \rangle$ and $\dfrac{A\psi\big(x_p\big)}{\psi\big(x_p\big)}$ are local energies.

3.1.1 Lattice VMC

For many-body Hamiltonians, we have a basis of configurations, that is, the Fock space basis. With increase in the number of atoms, the basis set grows exponentially. So Monte Carlo sampling is used to truncate this basis set. In case of lattice VMC, the states $|\psi\left(x_p\right)\rangle$ become the configurations $|\phi_i\rangle$ of the Fock space basis. The trial wave function would then be

$$|\Psi\rangle = \sum_j c_j|\phi_j\rangle$$

The weights of these configurations c_js are determined by the Gutzwillwer parameter[4].

Slater Determinants to Represent Many Body Wave Functions

The configurations are represented by Slater determinants. A Slater Determinant is written in the form

$$D = \frac{1}{\sqrt{N!}}\begin{vmatrix} \chi_1(\vec{x}_1) & \chi_2(\vec{x}_1) & \dots & \chi_N(\vec{x}_1) \\ \chi_1(\vec{x}_2) & & \dots & \\ & \ddots & & \\ & & \ddots & \\ \chi_2(\vec{x}_N) & \chi_2(\vec{x}_N) & \dots & \chi_N(\vec{x}_N) \end{vmatrix} \tag{3.3}$$

where $\chi_i(\vec{r_j})$ are the single electron functions. The electrons obey the Pauli exclusion principle and so they are anti-symmetric in nature. This antisymmetry is accounted for in the Slater Determinants. Let us denote the matrix of the Slater Determinant corresponding to the state $|\phi\rangle$ by $[\phi]$.

In general, a configuration $|\phi\rangle$ can be written as a direct product of the configuration with only ↑ electrons and that of only ↓ electrons

$$|\phi\rangle = |\phi_\uparrow\rangle \otimes |\phi_\downarrow\rangle$$

So that the corresponding Slater determinants can be written as

$$[\phi] = [\phi_\uparrow] \otimes [\phi_\downarrow]$$

But in VMC method, instead of taking the direct product we normally multiply the Slater Determinants in the RHS of the above equation to get the determinant for the full configuration, that is,

$$[\phi] \;=\; [\phi_{\uparrow}]\,[\phi_{\downarrow}]$$

Weights of the configurations: Gutzwiller parameter

This is a variational parameter which reduces the weights of those configurations having 'double occupancies'.
The Gutzwiller wave functions are given by

$$\begin{aligned} |\phi'\rangle &= \prod_i \{1 - (1-g)\, n_{i\uparrow} n_{i\downarrow}\} |\phi\rangle \\ &= g^{\langle n_{i\uparrow} n_{i\downarrow}\rangle} |\phi\rangle \end{aligned} \tag{3.4}$$

Thus Eq. 3.2 can be written as

$$\langle \hat{A} \rangle \;\approx\; \frac{1}{M} \sum_i \frac{A\phi'_i}{\phi'_i} \tag{3.5}$$

where $\phi'_i \;=\; \langle \phi'_i | \Psi_i \rangle$

The gutzwiller parameter g has to be optimized to get the expectation value of the energy nearest to the ground state.

3.1.1.1 The Trial Wave Function

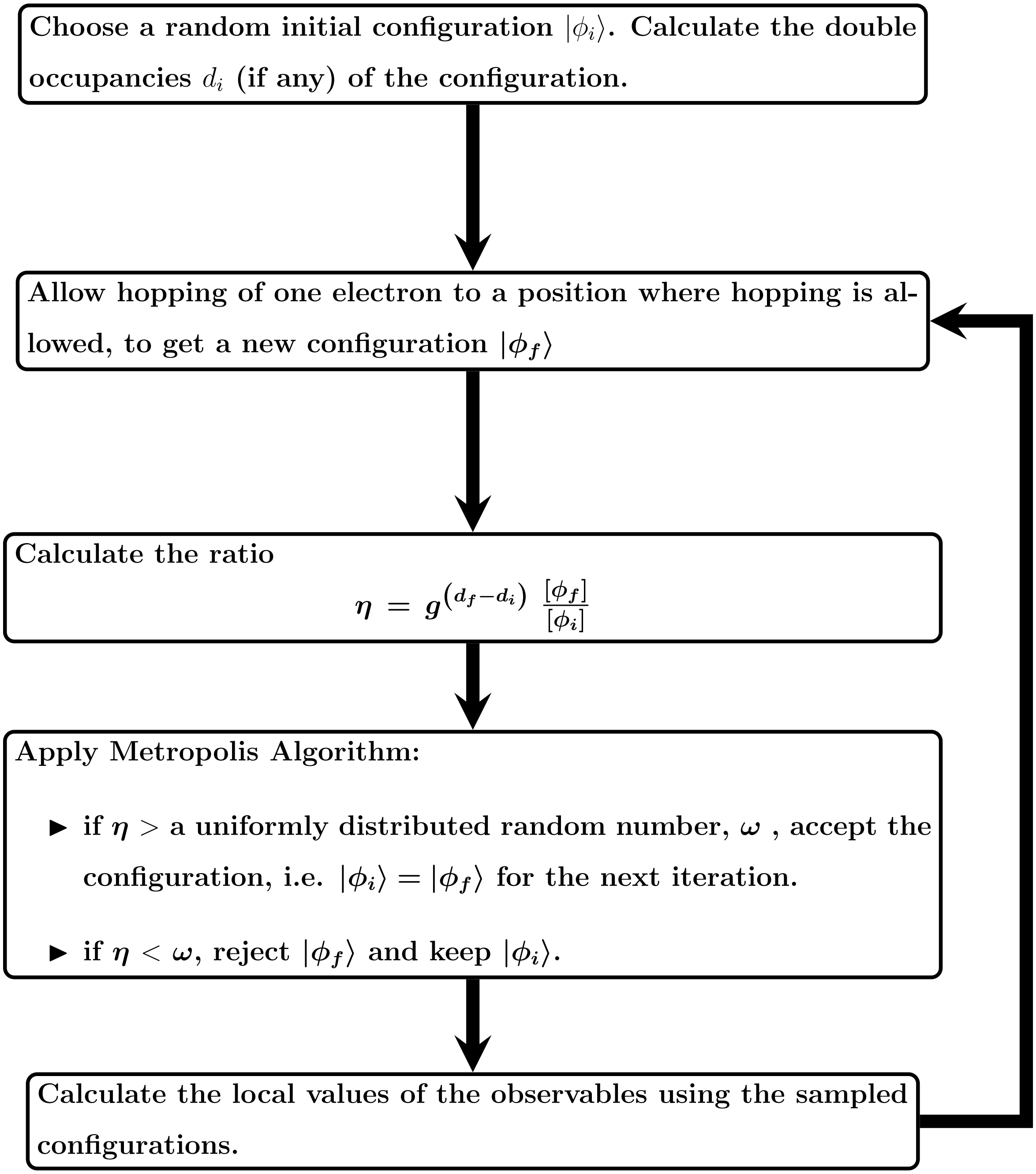
The ground state of the tight binding Hamiltonian (one without the Hubbard U term) is *Fermi sea* $|\Psi_{FS}\rangle$, which is actually the linear combination of all the possible configurations with *equal weights*.

$$|\Psi_{FS}\rangle \ = \ \frac{1}{\sqrt{N}}\sum_{j=N}|\phi_j\rangle \tag{3.6}$$

The trial wave function is taken to be the Fermi Sea wave function with double occupancies having reduced weights due to the Gutzwiller operator

$$|\phi'\rangle = \prod_i (1 - 1 - g)\, n_{i\uparrow}n_{i\downarrow})\, |\Psi_{FS}\rangle \tag{3.7}$$

So the following flowchart describes the steps.


Choose a random initial configuration $|\phi_i\rangle$. Calculate the double occupancies d_i (if any) of the configuration.
Allow hopping of one electron to a position where hopping is allowed, to get a new configuration $|\boldsymbol{\phi_f}\rangle$
Calculate the ratio $\boldsymbol{\eta} = \boldsymbol{g}^{\left(d_f - d_i\right)} \frac{[\phi_f]}{[\phi_i]}$
Apply Metropolis Algorithm:
▶ if $\boldsymbol{\eta} >$ a uniformly distributed random number, $\boldsymbol{\omega}$, accept the configuration, i.e. $|\phi_i\rangle = |\phi_f\rangle$ for the next iteration.
▶ if $\boldsymbol{\eta} < \boldsymbol{\omega}$, reject $|\phi_f\rangle$ and keep $|\phi_i\rangle$.
Calculate the local values of the observables using the sampled configurations.

3.1.1.2 Expression for the Local Energies

The expressions for the local energy for each configuration is given by[3]

$$E_{loc} \; = \; -t\sum_{j}\sum_{\sigma}\sum_{a} g^{\delta d}\frac{\det\left[\phi\left(\ldots, r_j + a, \ldots\right)\right]}{\det\left[\phi\left(\ldots, r_j, \ldots\right)\right]} + Ud \tag{3.8}$$

where δd is the change in the number of doubly occupied sites when the j^{th} electron at r_j hops to the position r_{j+a}. d is the total number of double occupancies.

3.1.2 Results

We have tried to develop a VMC code in FORTRAN for finite periodic as well as non-periodic systems and compared the accuracy of energy values with the exact diagonalization method. We are currently developing the VMC code for periodic system in momentum space.

3.2 Path Integral Renormalization Group (PIRG) Method

In this method[5,6], as discussed in the introduction, the imaginary time evolution operator $exp\{-\tau H\}$ is operated upon a trial wave function and after sufficiently large time, this is expected to give the ground state.

Similar to Feynman's path integral formalism, the above projection is performed in n steps of $\Delta\tau$ and then this $\Delta\tau$ is considered to be sufficiently small and $n \to \infty$ so that,

$$|\Psi_g\rangle \; = \; \lim_{\Delta\tau\to 0}\left(\lim_{n\to\infty} exp\{-\Delta\tau H\}\right)|\Psi_t\rangle$$

But, at every iteration of $\Delta\tau$, new basis states are generated. This increases the total number of basis states in each time step. This basis set is, however, truncated at each iteration, so that we get a *renormalized* basis set which is small enough to be handled computationally.

Suppose we take the Hubbard Hamiltonian.

$$\begin{aligned} H &= -t\sum_{\langle ij,\rangle\sigma}\left\{c_{i\sigma}{}^{\dagger}c_{j\sigma}+h.c.\right\}+U\sum_{i}n_{i\uparrow}n_{i\downarrow} \\ &= H_k \, + \, H_U \end{aligned}$$

The 1st term, H_k, contains 1-body operators $c_{i\sigma}{}^{\dagger}c_{j\sigma}$ and the 2nd term, H_U, which is the Hubbard term, has $n_{i\uparrow}n_{i\downarrow}$, where each term is a 2-body operator.

We can write the imaginary time evolution operator as

$$\begin{aligned} exp\{-\tau H\} &= exp\{-\tau\left(H_k+H_U\right)\} \\ &= exp\{-\tau H_k\}exp\{-\tau H_U\}+\mathcal{O}\left(\left(\Delta\tau^2\right)\right) \end{aligned} \tag{3.9}$$

The error $\mathcal{O}\left(\left(\Delta\tau^2\right)\right)$ comes because H_k and H_U do not commute.

We represent the wave functions as a linear combination of Slater determinants $|\phi\rangle$ as done in VMC.

$$D = \frac{1}{\sqrt{N!}}\begin{vmatrix} \chi_1\left(\vec{x}_1\right) & \chi_2\left(\vec{x}_1\right) & \ldots & \chi_N\left(\vec{x}_1\right) \\ \chi_1\left(\vec{x}_2\right) & & \ldots & \\ & \ddots & & \\ & & \ddots & \\ \chi_2\left(\vec{x}_N\right) & \chi_2\left(\vec{x}_N\right) & \ldots & \chi_N\left(\vec{x}_N\right) \end{vmatrix} \tag{3.10}$$

3.2.1 Effect of the hopping operator on Slater Determinants

Let us denote the matrix of the Slater Determinant corresponding to the state $|\phi\rangle$ by $[\phi]$. The matrix for the hopping operator can be obtained in the site basis without even considering the Fock basis. In general, the hopping matrix is a tridiagonal matrix, written as,

$$[K] \;=\; \begin{bmatrix} 0 & -t & 0 & \dots & 0 & \\ -t & 0 & -t & \dots & & 0 \\ & & \ddots & & & \\ & & & \ddots & & \\ & & & & -t & \\ & \dots & & -t & 0 & -t \\ 0 & 0 & & \dots & -t & 0 \end{bmatrix} \tag{3.11}$$

So the Slater Determinant can be modified directly by operating the hopping matrix $[K]$

$$[\phi'] \;=\; [K]\,[\phi']$$

which generates a *single* Slater determinant.

Similarly the operator $\exp\left([K]\right)$ will generate a single Slater determinant

$$[\phi'] \;=\; [M]\,[\phi']$$

where $\quad [M] \;=\; \exp\left([K]\right)$

3.2.2 Effect of one-body and two-body operators on Slater Determinants

Suppose there is a 2-body operator, $\sum\limits_{ij} \hat{O}_{ij}$, acting on the the Slater determinants.

Let us take the ‘diagonal term’ of the Slater determinant.

$$t_1 \;=\; \chi_1\left(\vec{r}_1\right)\chi_2\left(\vec{r}_2\right)\,\dots\,\chi_i\left(\vec{r}_i\right)\,\dots\,\chi_j\left(\vec{r}_j\right)\,\dots\,\chi_N\left(\vec{r}_N\right)$$

There is another term in this deteminant

$$t_2 \;=\; -\,\chi_1\left(\vec{r}_1\right)\chi_2\left(\vec{r}_2\right)\,\dots\,\chi_i\left(\vec{r}_j\right)\,\dots\,\chi_j\left(\vec{r}_i\right)\,\dots\,\chi_N\left(\vec{r}_N\right)$$

where the indices, i and j, are interchanged.

When $\hat{O}_{ij}$ acts on $(t_1 + t_2)$, it gives

$$\hat{O}_{ij}\left(t_1 + t_2\right) = \chi_1\left(\vec{r}_1\right)\chi_2\left(\vec{r}_2\right)\,\ldots\,\hat{O}_{ij}\begin{vmatrix}\chi_i\left(\vec{r}_i\right) & \chi_j\left(\vec{r}_i\right)\\ \chi_i\left(\vec{r}_j\right) & \chi_j\left(\vec{r}_j\right)\end{vmatrix}\ldots\,\chi_N\left(\vec{r}_N\right) \tag{3.12}$$

Thus each such pair of terms of indices i and j of the Slater Determinant give rise to a *new* Slater determinant when acted upon by the two body operator, $\hat{O}_{ij}$. This means that $\sum_{ij}\hat{O}_{ij}$, when acted on the Slater determinant, D, will give rise to many slater Determinants.

As we want to renormalize the basis set of Slater Determinants, we have to keep control over the number of Slater Determinants generated at each step.

For this we apply the *Hubbard Stratonovich* Transformation[7], on the two-body operator present in the Hamiltonian.

3.2.3 Applying the Hubbard-Stratonovich Transformation

The Hubbard Stratonovich transformation converts the fermionic interaction terms to non-interacting fermionic terms coupled to a fluctuating electric field[8]. The transformation formula is written as

$$exp\{\frac{1}{2}A^2\} \;=\; \int exp\left(\frac{1}{2}x^2 - xA\right)dx \tag{3.13}$$

where x is the fluctuating field.

The Hubbard term, can be written as

$$n_{i\uparrow}n_{i\downarrow} = \frac{1}{2}(n_{i\uparrow} - n_{i\downarrow})^2 \;-\; \frac{1}{2}(n_{i\uparrow} + n_{i\downarrow}) \tag{3.14}$$

If we define the auxillary field to be an Ising variable s, then it can be shown using Eq. 3.13 that,

$$\exp\{\Delta\tau U n_{i\uparrow} n_{i\downarrow}\} \;=\; \frac{1}{2}\sum_{s=\pm 1} \exp\{\alpha\,(s)\,n_{i\uparrow}\}\exp\{\alpha\,(-s)\,n_{i\downarrow}\} \tag{3.15}$$

where

$$\alpha\,(s) \;=\; 2as - \frac{\Delta\tau U}{2}$$

$$a \;=\; \tanh^{-1}\sqrt{\tanh\left(\frac{\Delta\tau U}{4}\right)}$$

The right hand side of Eq. 3.15 has 2 terms. So, this operator acting on a Slater determinant will generate 2 more Slater determinants.That is,

$$\exp\{\Delta\tau U n_{i\uparrow} n_{i\downarrow}\}|\phi\rangle \;=\; \frac{1}{2}\left(|\phi^{i+}\rangle + |\phi^{i-}\rangle\right) \tag{3.16}$$

So,

$$\begin{aligned}\exp\{\Delta\tau H_U\}|\phi\rangle &= \frac{1}{2^N}\prod_i \left(|\phi^{i+}\rangle + |\phi^{i-}\rangle\right)\\ &= \sum_j |\phi_j\rangle\end{aligned} \tag{3.17}$$

Thus this term would generate 2^N Slater Determinants at each time step, $\Delta\tau$. So this basis has to be truncated at every iteration. The truncation is performed by solving expectation values of the energies calculated with the old and the new basis sets. The one which gives the lower expectation value is considered for further calculation.

So the steps for the PIRG calculation are as follows

▶ STEP-1: **Choose an Initial Trial Wave Function**

We choose the trial wavefunction almost similarly as we do for Quantum Monte

Carlo Methods. We can also start with any random single Slater Determinant. After a number of iterations, we get a set of basis states $\{|\phi_i\rangle\}$ of size L (say) with which we construct trial wave function.

The trial wave function can then be written as

$$|\Psi_{trial}\rangle \;=\; \sum_{i=1}^{L} c_i|\phi_i\rangle \tag{3.18}$$

The c_is are taken as the Gutzwiller or Jastrow terms.

For example, if we consider the Gutzwiller parameter, g, each Slater Determinant $[\phi_i]$ (corresponding to the state $|\phi_i\rangle$) will become $g^{\langle n_{i\uparrow}n_{i\downarrow}\rangle}\,[\phi_i]$.

So we can calculate the expectation value $\frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}$ and minimize with respect to g .

▶ STEP-2: **Operate by $\exp\{\Delta\tau H_k\}$ on one of the Basis States**

Suppose the operator $\exp\{\Delta\tau H_k\}$ acts on the state $|\phi_j\rangle$. This will produce a single Slater Determinant $|\phi_j'\rangle$. So we have 2 basis sets: the old one is,

$$\{|\phi_1\rangle,\ |\phi_2\rangle\ \ldots\ ,|\phi_j\rangle\ \ldots\ ,|\phi_L\rangle\}$$

.

And the new one is

$$\{|\phi_1\rangle,\ |\phi_2\rangle\ \ldots\ ,|\phi_j'\rangle\ \ldots\ ,|\phi_L\rangle\} \qquad .$$

We calculate the expectation values $\dfrac{\displaystyle\sum_{mn} c_m^* c_n\langle\phi_m|\hat{H}|\phi_n\rangle}{\displaystyle\sum_{mn} c_m^* c_n\langle\phi_m|\phi_n\rangle}$ with both the basis sets and accept the one which gives the lower energy.

▶ STEP-3: **Operate by $\exp\{\Delta\tau H_U\}$ and Renormalize**

This itself is done in N steps, where N is the number of sites of the system.
$\exp(\Delta\tau n_{i\uparrow}n_{i\downarrow})$ will generate 2 Slater Determinants.
So there will be 3 basis sets to compare:

1. $\{|\phi_1\rangle, |\phi_2\rangle \ldots, |\phi_j\rangle \ldots, |\phi_L\rangle\}$
2. $\{|\phi_1\rangle, |\phi_2\rangle \ldots, |\phi_j^{i+}\rangle \ldots, |\phi_L\rangle\}$
3. $\{|\phi_1\rangle, |\phi_2\rangle \ldots, |\phi_j^{i-}\rangle \ldots, |\phi_L\rangle\}$

Now, the one which gives the lowest energy will be taken as the next basis set. The basis states $|\phi_j\rangle$, $|\phi_j^{i+}\rangle$ and $|\phi_j^{i-}\rangle$ from whichever basis set is chosen, is taken as the next state to operate on.
This step is repeated for $i = 1$ to n and every time the above comparison in made.

- ▶ STEP-4: **Repeat the above 3 steps till target energy converges**

Upto STEP-3 it was for one time step of $\Delta\tau$. The above steps are repeated till convergence ($|E_{j+1} - E_j|$ is less than some accuracy value of the order of 10^{-6}).

Using our PIRG code in FORTRAN, which is, in a stage of development, we plan to study accurately more correlated systems, which cannot be simulated using the DMRG method.

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