Exact solutions of generalized Hubbard Hamiltonian for diamond vacancies

Mehdi Heidari Saani∗, Mohammad Ali Vesaghi† and Keivan Esfarjani‡
Department of Physics, Sharif University of Technology,
Tehran, P.O.Box: 11365-9161, Iran

Abstract

A new formalism to calculate electronic states of vacancies in diamond has been developed using many-body techniques. This model is based on previous molecular models but does not use configuration interaction and molecular orbital techniques. A generalized Hubbard Hamiltonian which consists of all electron-electron interaction terms is calculated on the atomic orbital bases. Spatial symmetry $T_d$ and spin information of system are included in the form of Hamiltonian, so the eigenstates have automatically the correct spin and symmetry properties. Optimizing two key parameters of the model that justifies already reported semi-empirical values can predict accurate values of the famous absorption lines in neutral and charged vacancies i.e. $GR_1$ and $ND_1$. With these parameters the location of the low lying $^3T_1$ state is 113 mev above the ground state. In addition to these levels whole of the energy states of the system is predicted. Since the results are obtained without configuration interaction the model can gives the exact contribution of electronic configurations in the ground and excited states of the neutral and charged vacancies. The new results of the model for the ground and excited states of $GR_1$ are reported.

PACS numbers: 61.72.Bb, 61.72.Ji
I. INTRODUCTION

Vacancy is one of the simplest and familiar intrinsic point defects in semiconductors and its effects have attracted high technological and theoretical interests.\textsuperscript{1–3} A vacancy in diamond in contrast to the situation in most semiconductor or insulator crystals is stable in room temperature.\textsuperscript{4} Since the formation energy of vacancies in diamond is high (6 – 7 eV)\textsuperscript{5,6} they have been studied mainly in irradiated diamond. Optical absorption studies are used for determination of electronic excitation energies of vacancies\textsuperscript{7,8} and EPR, ENDOR experiments have been used for measuring the spin and spatial symmetry of electronic states.\textsuperscript{9–12} The most famous optical absorption lines in irradiated diamond are $GR_1$ (with zero phonon line at 1.673 eV)\textsuperscript{13} and $ND_1$ (with zero phonon line at 3.149 eV)\textsuperscript{14}. The former is attributed to a neutral vacancy\textsuperscript{15} and the latter to a negatively charged one.\textsuperscript{16}

In addition to these two famous lines many other absorption lines have been reported such as: $N_3$ (2.985 eV)\textsuperscript{8}, $H_3$ (2.463 eV)\textsuperscript{17}, $NV$ (1.945 eV)\textsuperscript{18} which have been attributed to vacancy-nitrogen\textsuperscript{19,20}, also $GR_2$ to $GR_8$ lines\textsuperscript{7} which have been attributed to the natural-charged vacancy complexes.\textsuperscript{21} Despite the simplicity of the system, different models have been suggested to explain the properties of these optical absorption lines. Generally there have been two main approaches to this problem, The first group of approaches are localized models\textsuperscript{22–26} and the second ones are extended models.\textsuperscript{27–31} In the first group, the electrons of the broken bonds which are in the tetrahedrally symmetric local potential of the vacant site are considered as an isolated molecule (many body approaches). In the second group i.e. extended models, the effect of lattice is more important on the vacancy and it is considered as a missing atom in a supercell with few hundreds of atoms (single particle approaches). Similarity between these two categories is their group theoretical aspects for accounting symmetries of the system while their main difference is in the importance of e-e
correlation effects. Lannoo and Bourgoin \cite{32} have developed a model with four parameters which brilliantly explains the validity range of the single and many particle approaches for this problem. According to Messmer and Watkins \cite{27} a successful model for describing vacancy energy states should explain the following points: The position of the defect energy levels relative to the valence band edge, the electronic wavefunction of defect electrons for comparing with experimental data, lattice relaxation and distortion in neighborhood of vacant site and it must be the basis of a practical computational scheme. The localized approaches have relatively successful answers to these questions.

The first suggested model in this regard is the famous model of the Coulson and Kearsly \cite{33}. Their model suggests a computational scheme that considers e-e interaction in the system accurately. They used group theoretical methods to manually construct symmetry and spin adapted wavefunctions for including spin and symmetry considerations of vacancies. By applying configuration interaction technique to the calculation results, they predicted qualitatively good results for electronic states of the vacancies, their model used two semi-empirical parameters to obtain satisfactory result for energy of the $GR_1$ transition. By using these semi-empirical parameters their predictions for $ND_1$ transiton and also the posision of the low lying $^3T_1$ state disagrees with available experimental data. Up to now this model has been the most successful computational scheme for describing physical properties of the optical absorption lines of vacancies in diamond,\cite{3,21} and the next suggested localized models\cite{21–26} are based on the framework of this model.

Localized models, unlike the nowadays commonly used density functional theory (DFT) methods which pay more attention on the ground state information, can also give the excitation energies of the vacancies beyond the one electron approximation.

For improving the quantitative agreement between theory and experiment we introduce a new approach for localized models. This approach is based on a gen-
eralized Hubbard Hamiltonian for electrons of the vacancy system with atomic orbital bases and uses computer adaptable many body techniques instead of usually used molecular orbital method (fourth item of messmer and watkins). In this paper at first we review the computational scheme of the present model and discuss the advantages of the new notation which is used for this problem. Then we apply this new scheme to solve generalized form of Hubbard Hamiltonian for neutral and charged vacancy systems. For evaluation of solutions of this Hamiltonian we start with parameters which were already reported. Our using value for the two semi-empirical parameters slightly differs from already reported values but other six parameters are as the same as the theory calculation. We report the effect of the hopping parameter on the energy spectrum of this Hamiltonian by varying this parameter.

The model predictions for \textit{GR1} and \textit{ND1} transitions with justified parameters and comparison the results with experimental data will be discussed. The location of the low lying \textit{3T_1} state is predicted and we discuss its comparison with other theoretical reports and experimental evidences. The results of our model can justify the semiempirical values that already were reported. We also will show that, this model is independent of familiar configuration interaction technique and the electronic configurations mixing of each state comes out in a natural manner from the formalism. The model predicts whole of the exact eigenstates and energy levels of the systems with the justified semi-empirical values. Finally the new information concerning electronic configurations of the ground and excited states of \textit{GR1} transition are reported which can be used by other approaches to this problem.

In our calculation the effects of lattice relaxation were ignored, which according to recent theoretical works are small.
II. COMPUTATIONAL MODEL

The present computational model takes into account electron correlation effects accurately and gives the correct spin and spatial symmetry of eigenstates. It is also suitable for small atomic cluster systems or molecules provided the hopping, Coulombic and exchange integrals are known. In the localized model framework, it is assumed that physical properties of neutral (charged) vacancy depend on four (five) electrons of adjacent dangling bounds. The exact Hamiltonian of such a system can be written as Eq. (1). A more simplified form of this Hamiltonian recently is applied to carbon nanotube systems \(^{36,37}\).

\[
H = \sum_{ij} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \frac{1}{2} \sum_{ijlm\sigma} V_{ijlm} c_{i\sigma}^\dagger c_{j\sigma}^\dagger c_{m\sigma} c_{l\sigma} \tag{1}
\]

Where \(i, j, l, m\) are atomic sites indices which go from 1 to 4 , \(\sigma\) is spin index which is \(-1/2\) or \(+1/2\) , \(c_{i\sigma}^\dagger\) and \(c_{i\sigma}\) are operators which create and annihilate electrons with specified spin \(\sigma\) on site \(i\). \(t_{ij}\) and \(V_{ijlm}\) parameters are hopping and \(e-e\) interaction overlap integrals which are defined as follows:

\[
t_{ij} = \int \int d\mathbf{r}' \psi_i^\ast(\mathbf{r}') (\frac{-\hbar^2}{2m} \nabla^2 + V(\mathbf{r})) \psi_j(\mathbf{r}) \tag{2}
\]

\[
V_{ijlm} = \int \int d\mathbf{r} d\mathbf{r}' \psi_i^\ast(\mathbf{r}') \psi_j^\ast(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_l(\mathbf{r}') \psi_m(\mathbf{r}') \tag{3}
\]

in the above integrals \(\psi_i\) is single electronic wave function in a specified site. The advantage of using second quantized form of Hamiltonian for this problem is its capability to include the spatial symmetry and spin information of the system in the form of Hamiltonian, hence the eigenstates have automatically the desired spin and symmetry properties. Also the effect of the changing each parameter directly can be observed on the electronic energy levels and also wave functions. This new approach uses atomic orbital bases to solve the Hamiltonian. In the previous localized models it was common as a start point, to manually construct symmetry and spin adapted molecular wave functions as
correct basis for accounting symmetry considerations of the system then these basis should be used in evaluating Hamiltonian matrix elements. This process is a laborious task and can not be incorporated in a computational software easily.

Unlike previous methods, present computational scheme needs significantly less effort and is straightforward in converting to computer software language. The starting point of the model is constructing appropriate many-body basis needed for solving the Hamiltonian.

All of the possible distribution of electrons in the four adjacent atomic orbital make a set of complete basis in the configuration space. In contrast to previous models that have used molecular orbital for such a system we have developed atomic orbital bases by taking into account $z$ component of the spin degree of freedom with occupation condition of each orbital. Following notation can be used to represent each configuration state. Ignoring the spin degree of freedom simply reduces the states to the occupation number or the Fock space representation. Fock space representation is commonly used in modern molecular calculations.\textsuperscript{39}

\begin{equation}
|\Psi_i > = |a_{i0}, a_{i1}, a_{i2}, ..., a_{i8} >
\end{equation}

Parameters $a_{i1}$ to $a_{i8}$ are -1 or +1 (for spin down and up on the site $i$ respectively) which show occupation condition of each state. In fact these coefficients not only show extension of electronic wave function on each neighboring site of vacancy but also include spin information of the system. $a_{i0}$ is the sum of all $a_i$'s i.e. the total spin of each $\Psi_i$ along $z$ axis. We will show the importance of this quantum number in our computation scheme later. Other capability of this notation is estimation of the maximum dimension of configuration space which one needs for calculating the Hamiltonian for $V^0 (V^-)$. In the $V^0 (V^-)$ system there are four (five) electrons respectively in four orbital, so the possible configurations of these electrons in the 8 accessible states (2 spin and 4 space
TABLE I: In this table, $S_{z}^{\text{tot}}$ is total spin in $z$ axis direction, $n_{up}$ is number of electrons with spin up and $n_{\Psi}$ is number of states with specific $S_{z}$.

| $S_{z}^{\text{tot}}$ | $V^0$ | $V^-$ |
|----------------------|-------|-------|
| +2                   | +1    | 0     |
| -2                   | +1/2  | -1/2  |
| +3/2                 | +1    | -2    |
| 0                    | 1     | 0     |
| 1                    | 4     | 3     |
| 2                    | 2     | 2     |
| 3                    | 1     | 1     |

| $n_{up}$ | $n_{\Psi}$ |
|----------|-------------|
| 4        | 16 36 16 1 |
| 3        | 4 24 24 4  |

The fractions of 70 (56) configuration states in $V^0$ ($V^-$) system which belong to each $S_z$ block are summarized in Table I. This counting method is in contrast to the old molecular orbital approaches which one needs to allow construction of symmetry and spin adapted basis by hand and then counting them.

After constructing the set of complete basis, we will calculate two form of Hamiltonian in this space. The first one is approximate form of Eq. (1), i.e. a simple extension of Hubbard model and the second is the exact form of the Hamiltonian (Eq. (1)) which we call it generalized Hubbard Hamiltonian.

### III. GENERALIZED HUBBARD HAMILTONIAN

The main goal of the Hubbard Hamiltonian is resuming atomistic nature of the solid besides the free electron gas theory. This model assumes that the most important part of $e-e$ interaction terms is on site term on the Columbic parts of Hamiltonian. The conventional form of this Hamiltonian consists of two parts, hopping term or $t$ term and on site term or $U$ term which is $V_{iii}$.
term of Eq. (3).

\[ H = \sum_{ij\sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \sum_i U_in_i \uparrow n_i \downarrow \]  

(7)

Famous Hubbard model with two parameters \( t \) and \( U \) is not sufficient for solving the vacancy problem, the results of our model with these two parameters are not satisfactory. This result is physically expecting since assuming only two parameters of the Hubbard model for this system means that the electrons interact with each other only when they are at the same site of at the same atom of the vacancy and this eliminates the interaction of the electrons when they are in the different atomic site of the vacancy. Therefore we started with extended Hubbard Hamiltonian with one extra parameter \( V \) which is \( V_{ijij} \) term of Eq. (3). This Hamiltonian is equivalent to the Lannoo model\textsuperscript{32} where the \( U \) parameter of their model is called \( V \) in our model. This means that the on site and two site direct overlap integrals are the most dominant ones and the rest parameters are negligible (Eq.(8)).

\[ H = \sum_{ij\sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \sum_i U_in_i \uparrow n_i \downarrow + \frac{1}{2} \sum_{i \neq j\sigma\sigma'} V_{ij} n_{i\sigma} n_{j\sigma'} \]  

(8)

Since the atomic sites in vacancy are from the vertex of a symmetrical tetrahedral, the distance between each two of them is the same, and hopping \( (t_{ij}) \), on site \( (U_i) \) and two site \( (V_{ij}) \) parameters of Hamiltonian are all independent of \( i, j \) indices and can be put outside of the sum Eq. (8).

\[ H = t \sum_{ij\sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_i \uparrow n_i \downarrow + \frac{1}{2} V \sum_{i \neq j\sigma\sigma'} n_{i\sigma} n_{j\sigma'} \]  

(9)

As discussed in sec. II, for \( V^0 \) \((V^-)\) system the size of the set which includes complete basis for solving this Hamiltonian is 70 (56). As a result solving Hamiltonian in this set results in a 70 \( \times \) 70 (56 \( \times \) 56) Hamiltonian matrix for \( V^0 \) \((V^-)\) respectively. As the starting point we used numerical values of Hamiltonian parameters \( t \), \( U \) and \( V \) which were reported by semi-empirical and theoretical works on diamond vacancies.\textsuperscript{33,41}
This formalism can investigate the effect of variation of each parameter on the energy spectrum directly. By this means we found that variation of parameter $t$ has not any effect on the $GR1$ transition energy. But variation of parameters $U$ and $V$ changes the transition energy of $GR1$. These variations do not affect the sequence of the levels. The results of calculation for $V^0$ show that for a wide variation range of variables, $t$ greater than $-12.5$ eV, $U$ greater than $8.2$ eV and $V$ greater than $4.0$ eV, the ground state of the system has $^1E$ symmetry (double degenerate spin-less) and we can obtain appropriate transition to an excited state $^1T_2$ (triple degenerate spin-less). With our model we were able to obtain the experimental value of $1.673$ eV for the GR1 transition.

For $V^-$ system, variation of $t$ has a dramatic effect on $ND1$ transition energy, but does not alter the ground and excited states sequence. Unlike this, $U$ and $V$ parameters which have only small effect on the values of the transition energies of the system. For the same range of variation of parameters we had a transition from $^4A_2$ ground state to a $^4T_1$ excited state ($ND1$ transition) but by the same parameters which we obtained the transition energy of $GR1$ ($1.673$ eV), there is a wide gap between the ground and excited states of $ND1$ transition (about $30$ eV).

Only with parameter $t$ close to $-1$ was the result close to the experimental value. This high value for $t$ seems unreasonable for the vacancy problem and is very far from reported range.$^{33,41}$

These results of the extended Hubbard Hamiltonian are in agreement with the results of the Lannoo and Bourgoin$^{32}$ model which has simplified the full Hamiltonian in the first quantization form by four parameters. They have used symmetrical molecular orbital base and also configuration interaction similar to Coulson and Kearsly model. The benefit of the reduction of the number of Hamiltonian parameter in their model was in this point that the validity range of single and many particle approaches could be investigated. They investigated the results of their model in a full range of parameters and also used the semi-
empirical parameters of the Coulson and Kearsly model. They successfully explained where the many body model works and where the single particle approaches can be valid. Lowther\textsuperscript{21} applied a similar model to the Lannoo model to explain some related optical phenomenon of the vacancies in diamond. Mainwood and Stonham\textsuperscript{26} applied Lannoo model directly to the vacancies electronic states in diamond. It seems that lack of the quantitative agreement with observed ND\textsubscript{1} transition energy (3.15 eV) from $^4A_2$ ground state to a $^4T_1$ excited state in $V^-$ system is due to elimination of exchange terms in Hamiltonian of vacancy system. Since calculation results of $V^-$ system show weaker agreement with the experiment than those for $V^0$, we can deduce that the role of the exchange terms in charged electron vacancy which has higher electron density is more important than that the four electron (neutral) one. Quantitative failure of the results of this simple extension of Hubbard Hamiltonian reveals that for vacancy system $e-e$ correlation effects are important and can not be neglected in contrast to the other cases which we are able to apply the Hubbard model. This point also was emphasized by previous models which have attempted diamond vacancy problem.\textsuperscript{21–26,33,41} Comparing numerical values of overlap integrals of Hubbard model\textsuperscript{40} and diamond vacancy problem\textsuperscript{33,41} (Table II) we find that the values of exchange integrals in this problem are comparable to the values of direct integrals so their elimination are not reasonable. This leads us to keep all of the, $t$, $U$ and $V$ terms besides exchange terms in four (neutral) and five (charged) electronic Hamiltonian of the system similar to Coulson and Kearsly model.\textsuperscript{33,41} We will call it generalized Hubbard Hamiltonian (Eq. (1)). Although this significantly increases the volume and complexity

| $V_{iij}$ | $V_{ijij}$ | $V_{iijj}$ | $V_{ijijk}$ | $V_{iiijj}$ |
|----------|-------------|-------------|-------------|-------------|
| Hubbard model\textsuperscript{40} (eV) | 20 | 2.3 | 0.5 | 0.1 | 0.025 |
| Diamond vacancies\textsuperscript{33,41} (eV) | 12.855 | 7.851 | 1.30 | 0.249 | 0.419 |

TABLE II: List of estimated Hamiltonian parameters in Hubbard model and diamond vacancies problem.
of the calculation, but since we take into account exact $e-e$ correlation effects, it makes our model more realistic.

We return to Hamiltonian form of Eq. (1). Similar symmetrical argument is valid for a system with $T_d$ symmetry and we can put hopping parameter ($t$) out of the sum (Eq. (10)).

$$H = t \sum_{ij\sigma} c_{i\sigma}^\dagger c_{j\sigma} + \frac{1}{2} \sum_{ijkl\sigma'}} V_{ijkl\sigma'} c_{i\sigma}^\dagger c_{j\sigma'}^\dagger c_{m\sigma'} c_{l\sigma}$$

(Symmetry of defect molecule, reduces the number of the independent parameters $V_{ijkl}$, from $4^4$ (256) components to only 7 independent ones, hence symmetry considerations can be included in the generalized form of Hamiltonian with a total of 8 parameters. These consist of the hopping $t$, two direct Coulombic integrals ($U,V$) and five exchange ($X1, ..., X5$) integrals as follows:

$$U = \langle ii | \frac{1}{r} | ii \rangle$$
$$V = \langle ij | \frac{1}{r} | ij \rangle$$
$$X1 = \langle ij | \frac{1}{r} | ji \rangle$$
$$X2 = \langle ii | \frac{1}{r} | ij \rangle$$
$$X3 = \langle ij | \frac{1}{r} | ik \rangle$$
$$X4 = \langle ii | \frac{1}{r} | jk \rangle$$
$$X5 = \langle ij | \frac{1}{r} | kl \rangle$$

Since the Hamiltonian is spin independent, useful conserving quantum numbers

$$[H, S^2] = [H, S_z] = 0$$

are total spin of four electron system ($S^2$) and the $z$ component of total spin ($S_z$). The important computational point about Eq. (11) is that it should hold for each arbitrary set of parameters of Eq. (10).
By these conservation rules we can easily decrease dimension of the nonzero block of Hamiltonian matrix by using conservation of total spin ($S^2$) and $z$ component of the total spin ($S_z$). Therefore the volume of calculation significantly reduces and matrix element evaluation only confines in subspaces where wave functions have the same values of $S_z$. As a result, the maximum dimension of nonzero matrix block in the case of $V^0$ ($V^{-}$) systems becomes 36 (24) respectively. The final step in solving the Hamiltonian of the $V^0$ ($V^{-}$) for obtaining the resultant eigenstates with definite $S_z$ and $S^2$ values is the transformation of Hamiltonian matrix from $S_z$ to ($S^2, S_z$) basis.

We have used the parameters which were calculated by Coulson and Larkins\textsuperscript{41} to investigate energy spectrum and eigenstates of the system. These parameters have been calculated using Slater and Clementi type functions as atomic orbitals.

The parameter calculation is independent from the Hamiltonian solution formalism. Since the parameters are calculated two times by the Coulson\textsuperscript{33,41} during a long period, other models similar to us have not attempted to re-estimate their values and all of them have used the results of the Coulson estimation for the parameters.\textsuperscript{21,22,26,32} The calculation of parameters were based on symmetric and antisymmetric molecular orbital basis ($a, t_x, t_y, t_z$) which were combinations of $a, b, c, d$ atomic orbitals. These atomic orbitals belong to the four nearest neighbor atoms of vacant site and are oriented inward to its center, however in the generalized Hubbard Hamiltonian Eq. (1), parameters are calculated directly by using overlap integrals of these $a, b, c, d$ atomic orbitals. These overlap integrals can be extracted from the older symmetric and anti-symmetric ones by changing the calculation basis. Related calculations have been performed and the resultant parameters are used in the computational scheme.
TABLE III: List of eight parameters that are needed to evaluate energy states of vacancy. They are estimated by this work and other different calculations.

| Parameter | Present model (eV) | Ref. 33, 41 (eV) | Ref. 41 (eV) |
|-----------|--------------------|------------------|-------------|
| $t$       | -7.74 13.58 7.85 0.41 2.18 0.25 1.30 0.215 | -8.12 12.85 7.85 0.41 2.18 0.25 1.30 0.25 | -7.13 12.85 7.85 0.64 2.66 0.35 1.56 0.32 |

IV. RESULTS AND DISCUSSION

The two key parameters of this model are $t$ and $U$. These two have been evaluated semi-empirically in the previous models and were starting point in calculation of the other parameters.\textsuperscript{33, 41} The reported values for hopping parameter $t$ cover a wide range of variations, for example both $-7.13$ eV and $-16.34$ eV values at the same time are reported for this parameter.\textsuperscript{33, 41} Concerning parameter $U$, the semi-empirical value is estimated to be 13.29 eV and after revising 12.85 eV while the theoretically calculated value is 19 eV.\textsuperscript{33, 41}

In evaluation of the $t$ parameter despite of other 7 Coulombic parameters, one not only need the information of the spatial distribution of the wave functions.

FIG. 1: Variation of ground $^1E$ and excited $^1T_2$ states of GR1 transition, with respect to hopping parameter $t$. The $t = -6.25$ eV, $-10.22$ eV are changing point of the ground state with $^3T_1$ state.
but also the form of the pseudopotential of carbon atoms is needed, so the uncertainty in the value of this is more than other parameters. In the present model the variation of the energy spectrum with $t$ has been investigated and results are shown in Fig. 1. The values of the other parameters are according to table III. According to this figure, for obtaining correct results for ground state of $V^0$ i.e. $^1E$, parameter $t$ should be confined in the following range.

$$-6.25eV \geq t \geq -10.22eV$$  \hspace{1cm} (12)

Choosing $t$ out of this range converts the sequence of two lowest states i.e. $^1E$ and $^3T_1$, and gives wrong ground state ($^3T_1$) for the system. Increasing value of the $t$ will lower the experimentally observed spin quintet $^5A_2$ state.\textsuperscript{11} It is interesting to note that above the upper limit of $t$, $^5A_2$ competes with $^3T_1$ to be the ground state and at $t$ value equals to $-5.96$ eV, $^5A_2$ becomes ground state of $V^0$ system. It seems that by increasing $t$ we reach an area where the Hund’s rule can be applied (according to this rule $^5A_2$ must be the ground state). This might be due to the point that $t$ is the indicator of the looseness of the electrons from the nuclei so by increasing $t$ we can consider the electrons as more delocalized electrons.

For charged vacancy case, the calculation results are shown in Fig.2. From this figure we conclude that for obtaining $^4A_2$ as ground state for the system, parameter $t$ should be restricted as:

$$-6.95eV \geq t \geq -16.34eV$$  \hspace{1cm} (13)

The lower limit is the negative of the ionization energy of electron in C-C bound of diamond. From this figure we can find that increasing $t$ over upper limit converts the ground state to $^4T_1$ which disagrees with the experiment.

By comparing the results of the calculation for both $V^0$ and $V^-$ we can put new
FIG. 2: Variation of ground $^4A_2$ and excited $^4T_1$ states of ND1 with respect to hopping parameters $t$. The $t = -6.95$ eV is changing point of the ground state with the excited state.

Boundaries to the single particle hopping parameter $t$ as follows:

$$-6.95 eV \geq t \geq -10.22 eV$$

(14)

This restriction on $t$ parameter, which is the most uncertain parameter in the vacancy electronic states problem, is tighter than already reported range ($-7.13$ eV to $-16.14$ eV).\textsuperscript{33,41} Variation of $t$ in this allowed range does not have significant effect on $GR_1$ transition energy. This is in agreement with other theoretical works.\textsuperscript{33,41} However this variation has a dramatic effect on $ND_1$ transition energy.

Numerical optimization of parameter $t$ in this range and also parameter $U$ gives $-7.747$ eV and $13.58$ eV for $t$ and $U$ respectively. These values are very close to the semi-empirically derived values by Coulson and Larkins (the difference between our optimized value by semi-empirical values in this two parameters are less than 8 and 5 percent respectively).\textsuperscript{41} Other six parameters are as the same as the theoretically calculated values by them using Slater type functions.\textsuperscript{41} Calculation methods of these parameters are completely independent from the Hamiltonian solution formalism so the previous models\textsuperscript{21,22,26,32} similar to us have used the parameters which are reported semi-empirically and theoretically by Coulson and Kearsly\textsuperscript{33} and Coulson and Larkins.\textsuperscript{41} These parameters are
calculated by them during a 17 year period and with the Slater type functions so it seems that the parameters are well justified. The difference between our suggested parameters with two semi-empirical parameters of their model is very less than the wide range of variation of these parameters in their model. (parameter \( t \) from \(-7.13\) eV to \(-16.34\) eV and parameter \( U \) which semi-empirically is \(12.855\) eV and theoretically is \(19\) eV)

With these justified values the present model can simultaneously obtain the exact transition energies of the \(GR1\) (1.67 eV) and \(ND1\) (3.15 eV) for neutral and charged vacancy system.

The set of our parameters and parameters that were previously computed based on Slater and Clementi type functions\(^{33,41,42}\) are listed in Table (III). The model predicts the wrong ground state with parameters which are based on Clementi type functions, i.e. \(3T_1\) instead of the experimentally observed \(^1E\) state for \(V^0\). This is similar to the Coulson and Larkins’s report.\(^ {41}\) However parameters which are based on the Slater type functions predict correct spin and symmetry for ground and excited states of \(GR1\) and \(ND1\) absorption lines but the values of the transition energies are not satisfactory. The results of the present model calculation are summarized in Fig. 3,4.

For neutral vacancy as it is shown in Fig. 3, there is a transition from double degenerate spinless ground state to a triple degenerate spinless excited state \((^1E \rightarrow ^1T_2)\) with a transition energy equal to 1.67 eV.

We also see that there is another level \(3T_1\), very close to \(^1E\) ground state with a very little energy difference i.e. about 113 meV above it. This value agrees with the recent experimental expectations which predict it will be more than 100 meV.\(^ {43}\) However the results of Coulson models gives 40 meV which disagree with the experiment.\(^ {33,41}\) This very close energy level to ground state also has been used to explain the behavior of \(R2\) center absorption line in
FIG. 3: Neutral vacancy energy levels with, $t = -7.747$ eV, $U = 13.58$ eV (present parameters) gives 1.673 eV for $^1E$ to $^1T_2$ transition. The right-hand side levels are the continuation of the left-hand side levels.

diamond where it was attributed to the strongly perturbed vacancy.\textsuperscript{42} By this assumption the energy difference of this level with the ground state has been predicted to be between 40 meV and 200 meV.\textsuperscript{42} Mainwood and Stonham\textsuperscript{26} have used the simple model of Lannoo\textsuperscript{31} and successfully explain many physical features of the vacancy. Lannoo for simplifying the problem do not enters the exchange parameters into energy levels and use only two parameters for describing energy levels. This is unlike to Coulson\textsuperscript{32,40} and our model which reserve whole of the e-e terms. Besides explaining many physical feature of the vacancy they gave some estimation for the position of this level. Using the model of Lannoo they positioned $^3T_1$ at 200 meV above the $^1E$, Although this value is as the same magnitude as the error in the positions of the levels in their calculations.\textsuperscript{26}

Our reported location for $^3T_1$ arises in a natural manner similar to $GR1$ and $ND1$ after evaluation of the exact Hamiltonian of the system with the justified parameters. The error which can be attributed to this value in our calculation is the difference between our parameters and semi-empirical parameters of the Coulson. This error is less than 8 percent which is significantly less than already reported error for the position of this level in similar calculations.\textsuperscript{26}
In obtaining this value we have not assumed that the vacancy is highly perturbed as it already was reported. This value can help EPR experimental investigations that expect to observe this state in temperatures higher than 300 K.

![Diagram showing negative vacancy energy levels]

**FIG. 4:** Negative vacancy energy levels with, $t = -7.747 \text{ eV}, U = 13.58 \text{ eV}$ (present parameters) gives $3.159 \text{ eV}$ for $^4A_2 \rightarrow ^4T_1$ transition. The right-hand side levels are the continuation of the left-hand side levels.

In the charged vacancy system, as it is shown in Fig. 4, the model predicts a transition from a non-degenerate ground state to a triple degenerate excited state with a spin equal to $3/2$ ($^4A_2 \rightarrow ^4T_1$). The energy difference is $3.15 \text{ eV}$ which is the famous observed $ND1$ absorption line. Previous models that evaluate e-e interaction exactly can not obtain this value by any set of parameters. In summary as it has been mentioned by other authors, the previous models that evaluate e-e interaction exactly can only explain GR1 transition energy quantitatively. They could not predict $ND1$ transition energy and also they have predicted the experimentally wrong energy for the low-lying $^3T_1$ level. These unsatisfactory quantitative results are obtained not only by the
semi-empirical parameters but also in a wide variation range of these two semi-empirical parameters.\textsuperscript{33,41} This variation ranges is very wider than the difference of our optimized values with semi-empirically reported ones for $t$ and $U$. Other six Coulombic parameters in our model and the previous ones are evaluated by theory.\textsuperscript{33,41} Our model can simultaneously give accurate transition energies for both of the $GR1$ and $ND1$ transitions besides the experimentally acceptable energy for the low-lying $^{3}T_1$ level with almost the same parameters (only two semi-empirical values differs less than 8 percent).

The results of our model have justified the Coulson and Kearsly semi-empirical parameters and also their guess\textsuperscript{32} which expected that the $t = -8$ eV value be more realistic than $t = -16.34$ eV. Both values of this parameter have been used in their models.\textsuperscript{33,41}

All of these qualitative and quantitatively satisfactory results in our model have obtained without configuration interaction. The good quantitative results for $GR1$ and even other reasonable qualitative results in the Coulson and Kearsly model and all of the previous molecular approaches\textsuperscript{22–26,32} can only be achieved with assistance of the Configuration interaction technique. This is for the first time that a molecular approach put aside the configuration interaction technique and could predict more experimental data. Configuration interaction has been widely used in all of the previous theoretical works to overcome the disagreement between theoretical results and experiment even at the qualitative levels.\textsuperscript{22–26,33,41,42} Although precise review of the previous exact models\textsuperscript{33,41} results on the charged vacancy with parameter $t = -16.34$ eV shows that applying configuration interaction gives wrong ground state for $V^{-}$.

Similar ambiguity also exists in the electronic configuration of the ground and excited state of the $GR1$. While the models assume that the ground and excited states of $GR1$ arise from the single configuration $a^2t^2$, at the same time they try to find or use some semi-empirically coefficients for the contribution of the other possible configurations in the ground and excited states of $GR1$.\textsuperscript{21,26} Here
we refer to Davies\textsuperscript{4} remark in this regard:
"The importance of configuration interaction at the vacancy in diamond was controversial, and alternative approaches were investigated in which emphasize was on the benefit of using large cluster".

The main advantages of the presented formalism which is based on molecular model is removing the configuration interaction besides it's satisfactory quantitative results. By this means our model have solved one important shortcoming of the molecular approaches with respect to cluster models or density functional approaches.

In the present model, the resultant eigenstates of the Hamiltonian have unique expansion on the starting constructed basis in configuration space, so configuration interaction comes out in a natural manner from the formalism. From this point, it is possible to find the contribution of each electronic configuration in ground and excited states of the system.

For $GR_1$ transition, the results of calculation for the ground state $^1E$ and the excited state $^1T_2$ with the justified parameters are illustrated in Fig. 5. The possible electronic configuration for states with value of $S = 0$ are: $(1,1,1,1), (2,1,1,0), (2,2,0,0)$ where the numbers in parenthesis show the occupation number of each tetrahedral orbital of vacancy system. As it is shown in Fig. 5,

all possible electronic configurations are present in the ground state $^1E$. The most probable configuration in ground state arise from $(1,1,1,1)$ configuration (61 percent) which has only singly occupied orbitals. Two doubly occupied configurations have very low contribution (3 percent) in the ground state. In $(1,1,1,1)$ configuration the electrons have maximum separation distance, which results in lowering the Coulombic repulsion energy of the system. In contrast to this, the excited state of $GR_1$, i.e. $^1T_2$ is orthogonal to $(1,1,1,1)$ configuration and is almost a purely doubly occupied configuration state. This configuration
FIG. 5: Percentage of the contribution of each possible electronic configuration in ground and excited state of GR1 transition for neutral vacancy system, the numbers in parenthesis are occupation number of each tetrahedral orbital.

As the results of our calculation show, the absence of (1, 1, 1, 1) configuration in the ground state of the system is unexpected, since it has minimum Coulombic repulsion energy among the other configurations of the system. Also it is the only compatible configuration of the unique $^5A_2$ excited state, which in the delocalization limit ($t > -5.96$ eV) is the ground state of the system.

For ND1 transition, since the ground and exited states have the spin equal to 3/2 the only configuration which can be encountered is (2, 1, 1, 1). Therefore the ground and excited states are only a combination of these configurations with different $S_z$ values and the results are same as other models.

The new information about the ground and excited state of the GR1 is
very important, it can open a new opportunity for ab-initio density functional approaches which have not been attempted to estimate the value of this transition.\textsuperscript{35} This is due to the results of the previous molecular orbital models which have assumed the ground and excited state belong to the same configuration $a^2t^2$. However by the new result of present model, they can try to obtain the transition energy of the $GR1$ transition similar to $ND1$. These information are also useful for theoretical approaches which start from a guess wave function for ground and excited states of such a molecular system.

V. CONCLUSION

Theoretical studies of the vacancy electronic states in diamond have been a challenging problem for the five decades. Localized models which originate from Coulson and Kearsly pioneering work, predict correctly the spatial symmetry and spin of electronic states but can not give quantitatively good results for electronic transitions in diamond vacancies. In their model despite of excellent theoretical framework and strong physical intuition, the computational method are very old and can not be adapted with nowadays powerful computer assisted methods.

We have developed a new approach based on generalized Hubbard Hamiltonian and many body techniques. A complete set of atomic orbital basis for describing this system is constructed according to $S_z$ representation of each electronic configuration in the four vacancy orbital. This confines the calculation only in definite $S_z$ subspace. This representation can simply estimate number of states of the system and also each definite $S_z$ block size of Hamiltonian. This is in contrast to previous models that uses molecular orbital bases and manually construct each symmetry and spin adapted wave functions.

The generalized Hubbard Hamiltonian which contains whole of the $e-e$ correlation terms is included with spatial symmetry information of the vacancy
therefore the number of the independent parameters of the Hamiltonian is reduced to 8. By this means the effect of the parameters on the energy states directly can be examined. A detailed computer software is developed to solve this Hamiltonian. The resultant Hamiltonian matrix is transformed to change basis from $S_z$ to $S^2$ representation. As the result, the eigenstates have definite and correct spin and symmetry properties.

The effect of changing each Hamiltonian parameters on the electronic states of the system directly can be examined. This calculation shows that for obtaining experimentally correct results for the ground state of $V^0$ and $V^-$, parameter $t$ should be in the $-10.22$ eV to $-6.95$ eV range, although increasing $t$ in this range has low effect on $GR1$ but significantly increases $ND1$ transition energy. According to this model the optimum value for two key semi-empirical parameters $t$ (in allowed range) and $U$ are $-7.747$ eV, $13.58$ eV respectively. Two famous absorption lines of $V^0$ and $V^-$ namely $GR1$ (1.67 eV) and $ND1$ (3.15 eV) can be obtained simultaneously and exactly with these parameters in addition to the location of the low-lying $^3T_1$ state at 113 meV above the ground state of the $V^0$. These results have been obtained for the time by such justifiable parameters. These parameters also justify already reported semi-empirical values that only could estimate $GR1$ transition and gave experimentally wrong results for $^3T_1$.

For the first time the configuration interaction procedure, has not used in such a calculations and it arises in a natural from from the formalism. Despite of its ambiguous physical nature, the configuration interaction techniques plays a fundamental and vital role in reaching to an agreement with experimental data in previous localized models. This vital role even exist at the level of qualitatively acceptable results. This point enables us to estimate the contribution of each electronic configuration in ground and excited states of the system. The results for $GR1$ absorption line show that it is almost a transition from configurations that consist of a pure singly occupied orbital and a singly
double occupied orbital to a singly occupied orbital configuration. This new information can be used by the density functional approach to this problem. The results of our model justifies the first suggested molecular model by the Coulson and Kearsly is the five decades ago and shows that their model has enough physical depth to accompany with a new computational methods to obtain very satisfactory quantitative results. The results also show the benefit of the localized models with respect to cluster or density functional approaches by no need of configuration interaction.

VI. ACKNOWLEDGMENT

We would like to thanks Dr.A. Shafikhani and Mr.M. Sariai for their valuable comments about this work. We acknowledge the help of Mr.A. Rezakhani(Phd student) and Mr.M. Ghasempour for computer programming and paper preparation.

*e-mail: Heydaris@mehr.sharif.edu
†e-mail: Vesaghi@sharif.edu
‡e-mail: K1@sharif.edu

[1] S. Goedecker, T. Deutsch and L. Billard, *Phys. Rev. Lett.* **88**, 235501 (2002)
[2] T. Miyazaki and H. Okushi, *Appl. Phys. Lett.* **78**, 25 (2001).
[3] U. Gerstmann, M. Amkreutz and H. Overhof, *Phys. Rev. B* **60**, 8446 (1999).
[4] G. Davies and N. B. Manson, in *Properties and growth of diamond*, edited by G.Davies (IEE, London 1994), p.159
[5] S. P. Mehandru, A. B. Anderson and J. C. Angus, *J. Mater. Res.* **7**,689 (1992)
[6] J. Bernholc, A. Antonelli, T. M. DelSole, Y. Bar-Yam, S. T. Pantelides, \textit{Phys. Rev. Lett.} \textbf{61}, 2689 (1993).

[7] N. B. Manson, J. Porsch and W. A. Runciman, \textit{J. Phys. C} \textbf{13} (1980).

[8] I. N. Douglas and W. A. Runciman, \textit{Phys. Chem. Miner. (Germany)} \textbf{1} (1977).

[9] I. N. Douglas and W. A. Runciman, \textit{J. Phys. C} \textbf{10}, 2253 (1993).

[10] J. Isoya, H. Kanda, Y. Uchida, S. C. Lawson, S. Yamasaki, H. Itoh, Y. Morita, \textit{Phys. Rev. B} \textbf{45}, 1436 (1992)

[11] J. A. Vanwyk, O. D. Tucker, M. E. Newton, J. M. Baker, G. S. Woods and P. Spear, \textit{Phys. Rev. B} \textbf{52}, 17 (1995)

[12] J. E. Lowther and J. A. VanWyk, \textit{Phys. Rev. B} \textbf{49}, 11010 (1994)

[13] C. D. Clark, R. W. Ditchburn and H. B. Dyer, \textit{Proc. Roy. Soc.} \textbf{234} (1956).

[14] H. B. Dyer and L. du. Preez, \textit{J. Chem. Phys.} \textbf{42} (1956).

[15] J. Walker, \textit{Rep. Prog. Phys.} \textbf{42}, 1605 (1978).

[16] G. Davis, \textit{Nature} \textbf{269}, 498 (1977)

[17] A. T. Collins, G. Davies, H. Kanda and G.S. Woods, \textit{J. Phys. C} \textbf{21} (1988).

[18] N. R. S. Reddy, N. B. Manson and E. R. Krausz, \textit{J. Lumin. (Netherland)} \textbf{38} (1987).

[19] G. Davies and M. F. Harmer, \textit{Proc. R. Soc. London}, Ser. A \textbf{348}, 285 (1976)

[20] J. E. Lowther, \textit{J. Phys. Chem. Solids} \textbf{45}, 127 (1984)

[21] J. E. Lowther, \textit{Phys. Rev. B} \textbf{48}, 11592 (1993)

[22] J. Fridell, M. Lanoo and G. Leman, \textit{Phys. Rev.} \textbf{164}, 1056 (1967)

[23] T. Yamagouchi, \textit{J. Phys. Soc. Jpn.} \textbf{17}, 1359 (1962)

[24] W. E. Hogstone, \textit{J. Phys. C} \textbf{3}, 791 (1969)

[25] A. M. Stoneham, \textit{Proc. Phys. Soc.} \textbf{88}, 135 (1966)

[26] A. Mainwood, A. M. Stonham, \textit{J. Phys. Condensed matter} \textbf{9}, 2453 (1997).

[27] R. P. Messmer and G. D. Watkins, \textit{Phys. Rev. B} \textbf{7}, 2568 (1973).

[28] F. P. Larkins, \textit{J. Phys. Chem. Solids} \textbf{23}, 965 (1976).

[29] A. Mainwood, \textit{J. Phys. C} \textbf{11}, 2703 (1978).
[30] R. P. Watkins, G. D. Watkins, *Phys. Rev. Lett.* **32**, 1244 (1975).
[31] G. B. Bachelet, G. A. Baraff and M. Schluter, *Phys. Rev. B* **24**, 4736 (1981).
[32] M. Lannoo and J. Bourgoin, *in point defects in semiconductors, I, Theoretical Aspects*, (Springer, Berlin 1981), p. 141
[33] C. A. Coulson and M. J. Kearsly, *Proc. R. Soc.* **241**, 433 (1957)
[34] L. H. Li and J. E. Lowther, *Phys. Rev. B* **53**, 11277 (1996)
[35] S. J. Breuer and P. R. Briddon, *Phys. Rev. B* **51**, 6984 (1995)
[36] A. Zywietz, J. Furthmuller and F. Bechstedt, *Phys. Status. Solidi B* **210**, 13 (1998)
[37] A. Farajian, K. Esfarjani, Y. Kawazoe, *Phys. Rev. Lett.* **82**, 25 (1999)
[38] A. Farajian, K. Esfarjani, M. Mikami, *Phys. Rev. B* **65**, 165415 (2002)
[39] T. Helgaker, P. Jorgenssen and J. Olsen, *in Molecular electronic structure theory*, (John wiely and Sons, 2000), p. 8
[40] J. Hubbard, *Phys. Rev. Lett.* **10**, 5 (1963)
[41] C. A. Coulson and F. P. Larkins, *J. Phys. Chem. Solids* **32** (1971)
[42] A. Mainwood, J. E. Lowther and J. A. Van Wyk, *J. Phys. Condens. Matter* **5**, (1993)
[43] D. J. Twitchen, M. E. Newton, J. M. Baker and V. A. Nadolny, *in Properties, growth and application of diamond*, edited by M. H. Nazare and A. J. Neves (IEE, London 2001), p. 214
[44] J. E. Lowther, *in Properties, growth and application of diamond*, edited by M. H. Nazare and A. J. Neves (IEE, London 2001), p. 179
[45] G. Davies, *in Properties, growth and application of diamond*, edited by M. H. Nazare and A. J. Neves (IEE, London 2001), p. 193