# Exact solution of the Hubbard model for a four-center tetrahedral cluster

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The eigenvalues of a Hubbard Hamiltonian for a four-center tetrahedral cluster are calculated exactly. Full use is made of the symmetry of the problem, which is analyzed for an arbitrary number of electrons, $0 \leq N \leq 8$. Comparison is made with the phenomenological Hund's-rule predictions for the ground states. The diversity of the low-energy states is surprising: magnetic and nonmagnetic solutions, single and degenerate representations, accidental degeneracies, and symmetry crossovers are all found for the ground states. Implications for three-dimensional lattices are discussed.

## I. INTRODUCTION

Hubbard's model has become, since its introduction[1] in 1963, the most popular example of a system of interacting electrons with short-range interactions. It has been used in the literature to study a great variety of many-body effects in metals, of which ferromagnetism, antiferromagnetism, metal-insulator transitions, spin-density waves, and charge-density waves are the most common examples.[1–6]

The model has been applied to a variety of lattices, one, two, and three dimensional,[2,3,7] and occasionally to small clusters.[8] Exact solutions are available in very few instances[7,8] and general theorems[9] have been proved for some cases. With all this activity, however, exact solutions are not possible for most systems, and some of the approximations found in the literature remain, at best, appealing conjectures or blind tries.[10,11]

The object of this paper is to solve exactly a very simple system, simple enough to allow an exact solution, but with enough complexity to shed light into the physics of real systems. We have chosen the case of a four-atom cluster of tetrahedral symmetry, given by the Hamiltonian

$$H=(-t)\sum_{i,j,\sigma} c_{i\sigma}^{\dagger}c_{j\sigma}+U\sum_{i} c_{i\uparrow}^{\dagger}c_{i\uparrow}c_{i\downarrow}^{\dagger}c_{i\downarrow}\ , \tag{1.1}$$

where $c_{i\sigma}$ ($c_{i\sigma}^{\dagger}$) is the annihilation (creation) operator for an electron of spin $\sigma$, located at the site $i$ of the tetrahedral cluster ($i,j=1,2,3,4$). For the sake of simplicity we consider only the case of non-negative $t$, $t \geq 0$, which corresponds to attractive nuclear potentials ($s$ orbitals lower in energy than $p$ orbitals). We, however, allow the interaction constant $U$ to take any value, positive or negative. In this fashion we include in our calculation not only the magnetic cases ($U>0$), but also charge-density waves and polar states ($U<0$).

Several aspects of this model deserve discussion from the start.

(a) It is identical to the Hamiltonian of the infinite face-centered-cubic lattice if the Brillouin-zone sampling is restricted to four reciprocal-lattice points, the zone center $\Gamma$, and the three square-face-center points $X$.

(b) Since the four one-electron orbitals which diagonalize the first term in (1.1) are one $s$-like orbital, of energy $\epsilon_s=-3t$, and three $p$-like orbitals, of energy $\epsilon_p=t$, there is a marked electron-hole asymmetry in the one-electron spectrum. This asymmetry is characteristic of odd-numbered rings (triangular rings in this case), and typical of the closed-packed faced-centered-cubic and hexagonal lattices. The asymmetry brings new features into the spectrum and carries with it a more interesting, less symmetric, half-filled band.

(c) It is also possible to think of this system as an atom for which only the $s^n p^m$ configurations ($0 \leq n \leq 2$, $0 \leq m \leq 6$) are possible and with $\epsilon_s < \epsilon_p$. Under these conditions the usual techniques of atomic physics, Hund's rule in particular,[12,13] can be applied, and their results compared with the exact solution. As we find out, agreement and exceptions are both encountered.

(d) The presence or absence of magnetic solutions for the ground states are both instructive and in some instances surprising. The main conclusion to extract from these calculations is that Hubbard's model exhibits a richness of structure in its solutions which defies easy global generalizations. In its variety it permits the mimicking, albeit poorly, of many electronic and magnetic phases found in real transition metals.

Our problem is greatly simplified by systematic application of group theory. As a result the most complicated equation to solve for the eigenvalues is a cubic equation, i.e., the complete problem can be solved analytically. Our procedures and solutions are given in Sec. II.

TABLE I. Character table of $T_d$.

| | 1 $E$ | 3 $C_2$ | 8 $C_3$ | 6 $\sigma$ | 6 $S_4$ | Atomic symmetries |
|---|---|---|---|---|---|---|
| $\Gamma_1$ | 1 | 1 | 1 | 1 | 1 | $s_g$ |
| $\Gamma_2$ | 1 | 1 | 1 | −1 | −1 | $s_u$ |
| $\Gamma_3$ | 2 | 2 | −1 | 0 | 0 | $d_g d_u$ |
| $\Gamma_4$ | 3 | −1 | 0 | 1 | −1 | $p_u d_g$ |
| $\Gamma_5$ | 3 | −1 | 0 | −1 | 1 | $p_g d_u$ |

 

TABLE II. Configurations, symmetries and eigenvalues in the noninteracting limit $U=0$.

| $N$ | States | Levels | Configuration | Energy | Symmetries |
|---|---|---|---|---|---|
| 0 | 1 | 1 | | 0 | $^1\Gamma_1$ |
| 1 | 2 | 1 | $s^1$ | $-3t$ | $^2\Gamma_1$ |
| 1 | 6 | 1 | $p^1$ | $t$ | $^2\Gamma_4$ |
| 2 | 1 | 1 | $s^2$ | $-6t$ | $^1\Gamma_1$ |
| 2 | 12 | 2 | $s^1p^1$ | $-2t$ | $^1\Gamma_4$ $^3\Gamma_4$ |
| 2 | 15 | 4 | $p^2$ | $2t$ | $^1\Gamma_1$ $^1\Gamma_3$ $^1\Gamma_4$ $^3\Gamma_5$ |
| 3 | 6 | 1 | $s^2p^1$ | $-5t$ | $^2\Gamma_4$ |
| 3 | 30 | 5 | $s^1p^2$ | $-t$ | $^2\Gamma_1$ $^2\Gamma_3$ $^2\Gamma_4$ $^2\Gamma_5$ $^4\Gamma_5$ |
| 3 | 20 | 4 | $p^3$ | $3t$ | $^2\Gamma_3$ $^2\Gamma_4$ $^2\Gamma_5$ $^4\Gamma_2$ |
| 4 | 15 | 4 | $s^2p^2$ | $-4t$ | $^1\Gamma_1$ $^1\Gamma_3$ $^1\Gamma_4$ $^3\Gamma_5$ |
| 4 | 40 | 8 | $s^1p^3$ | 0 | $^1\Gamma_3$ $^1\Gamma_4$ $^1\Gamma_5$ $^3\Gamma_2$ $^3\Gamma_3$ $^3\Gamma_4$ $^3\Gamma_5$ $^5\Gamma_2$ |
| 4 | 15 | 4 | $p^4$ | $4t$ | $^1\Gamma_1$ $^1\Gamma_3$ $^1\Gamma_4$ $^3\Gamma_5$ |
| 5 | 20 | 4 | $s^2p^3$ | $-3t$ | $^2\Gamma_3$ $^2\Gamma_4$ $^2\Gamma_5$ $^4\Gamma_2$ |
| 5 | 30 | 5 | $s^1p^4$ | $t$ | $^2\Gamma_1$ $^2\Gamma_3$ $^2\Gamma_4$ $^2\Gamma_5$ $^4\Gamma_5$ |
| 5 | 6 | 1 | $p^5$ | $5t$ | $^2\Gamma_4$ |
| 6 | 15 | 4 | $s^2p^4$ | $-2t$ | $^1\Gamma_1$ $^1\Gamma_3$ $^1\Gamma_4$ $^3\Gamma_5$ |
| 6 | 12 | 2 | $s^1p^5$ | $2t$ | $^1\Gamma_4$ $^3\Gamma_4$ |
| 6 | 1 | 1 | $p^6$ | $6t$ | $^1\Gamma_1$ |
| 7 | 6 | 1 | $s^2p^5$ | $-t$ | $^2\Gamma_4$ |
| 7 | 2 | 1 | $s^1p^6$ | $3t$ | $^2\Gamma_1$ |
| 8 | 1 | 1 | $s^2p^6$ | 0 | $^1\Gamma_1$ |

## II. CALCULATION AND RESULTS

Since there are eight spin orbitals in the system, and each one can be either empty or occupied by an electron, we have altogether $2^8=256$ possible eigenstates of (1.1). Since the number $N$ of electrons is conserved, and $0\leq N\leq 8$, for a given $N$ there are $[8!/N!(8-N)!]$ eigenstates.

These eigenstates can be classified according to their spin and their spatial symmetries. Since the spin degree of freedom is conserved by (1.1), the states can be labeled as spin singlets, doublets, triplets, quartets, and quintets. The symmetry of the spatial part of the Hamiltonian is defined by its point group, which in this case is the full tetrahedral group $T_d$, of 24 elements. The character table of this group is given in Table I. Also included in Table I are the atomiclike symmetries of the various representations of $T_d$.

An analysis of the levels and energies in the two extreme limits is presented in Tables II and III. Table II is for the noninteracting limit (finite $t$, vanishing $U$), in which the energy levels depend only on the configuration $s^np^m$. The 256 states divide into 21 configurations which encompass the 56 distinct levels of the full tetrahedral symmetry. Table III is for the strongly interacting limit (finite $U$, either positive or negative, vanishing $t$). There the 256 states and 56 levels coalesce into 15 energy levels. From either table it can be seen that $N$-number, spin, and

TABLE III. Symmetries and eigenvalues in the strongly interacting limit $t=0$.

| $N$ | States | Levels | Energy | Symmetries |
|---|---|---|---|---|
| 0 | 1 | 1 | 0 | $^1\Gamma_1$ |
| 1 | 8 | 2 | 0 | $^2\Gamma_1$ $^2\Gamma_4$ |
| 2 | 24 | 5 | 0 | $^1\Gamma_1$ $^1\Gamma_3$ $^1\Gamma_4$ $^3\Gamma_4$ $^3\Gamma_5$ |
| 2 | 4 | 2 | $U$ | $^1\Gamma_1$ $^1\Gamma_4$ |
| 3 | 32 | 5 | 0 | $^2\Gamma_3$ $^2\Gamma_4$ $^2\Gamma_5$ $^4\Gamma_2$ $^4\Gamma_5$ |
| 3 | 24 | 5 | $U$ | $^2\Gamma_1$ $^2\Gamma_3$ $^2\Gamma_4$ $^2\Gamma_4$ $^2\Gamma_5$ |
| 4 | 16 | 3 | 0 | $^1\Gamma_3$ $^3\Gamma_5$ $^5\Gamma_2$ |
| 4 | 48 | 10 | $U$ | $^1\Gamma_1$ $^1\Gamma_3$ $^1\Gamma_4$ $^1\Gamma_4$ $^1\Gamma_5$ $^3\Gamma_2$ $^3\Gamma_3$ $^3\Gamma_4$ $^3\Gamma_5$ $^3\Gamma_5$ |
| 4 | 6 | 3 | $2U$ | $^1\Gamma_1$ $^1\Gamma_3$ $^1\Gamma_4$ |
| 5 | 32 | 5 | $U$ | $^2\Gamma_3$ $^2\Gamma_4$ $^2\Gamma_5$ $^4\Gamma_2$ $^4\Gamma_5$ |
| 5 | 24 | 5 | $2U$ | $^2\Gamma_1$ $^2\Gamma_3$ $^2\Gamma_4$ $^2\Gamma_4$ $^2\Gamma_5$ |
| 6 | 24 | 5 | $2U$ | $^1\Gamma_1$ $^1\Gamma_3$ $^1\Gamma_4$ $^3\Gamma_4$ $^3\Gamma_5$ |
| 6 | 4 | 2 | $3U$ | $^1\Gamma_1$ $^1\Gamma_4$ |
| 7 | 8 | 2 | $3U$ | $^2\Gamma_1$ $^2\Gamma_4$ |
| 8 | 1 | 1 | $4U$ | $^1\Gamma_1$ |

TABLE IV. Symmetry of the ground states.

| $N$ | Configuration | Hund's-rule symmetry | Symmetry $U>0$ | Symmetry $U<0$ |
|---|---|---|---|---|
| 0 | | $^1\Gamma_1$ | $^1\Gamma_1$ | $^1\Gamma_1$ |
| 1 | $s^1$ | $^2\Gamma_1$ | $^2\Gamma_1$ | $^2\Gamma_1$ |
| 2 | $s^2$ | $^1\Gamma_1$ | $^1\Gamma_1$ | $^1\Gamma_1$ |
| 3 | $s^2p^1$ | $^2\Gamma_4$ | $^2\Gamma_4$ | $^2\Gamma_4$ |
| 4 | $s^2p^2$ | $^3\Gamma_5$ | $^1\Gamma_3$ | $^1\Gamma_1$ |
| 5 | $s^2p^3$ | $^4\Gamma_2$ | $^4\Gamma_2$ | $^2\Gamma_3$ |
| 6 | $s^2p^4$ | $^3\Gamma_5$ | $^1\Gamma_3\oplus{}^3\Gamma_5$ | $^1\Gamma_1$ |
| 7 | $s^2p^5$ | $^2\Gamma_4$ | $^2\Gamma_4$ | $^2\Gamma_4$ |
| 8 | $s^2p^6$ | $^1\Gamma_1$ | $^1\Gamma_1$ | $^1\Gamma_1$ |

space symmetries reduce the problem to a completely analytic one, with at most a $(3\times3)$ secular equation to solve for a given energy level.

If our system for the case of repulsive interactions is considered as a "structured" atom, it should be possible to apply to it Hund's empirical rule,[12,13] which states that for a given $N$ the ground-state level is determined by (1) selecting the lowest-energy configuration, (2) selecting the largest spin-multiplicity out of the levels in that configuration, and (3) selecting from those the term of the largest angular momentum $L$, if (2) leaves more than one level.

An examination of Table II yields the results shown in the first three columns of Table IV. It can be seen that $N=4$, 5, and 6 are predicted by Hund's rule to yield magnetic states, i.e., ground states with spin multiplicities other than singlets or Kramers doublets.

The group-theory factorization and the calculation of the matrix elements of (1.1) yield the 37 secular equations given in Table V. These equations reduce, as expected, to the results of Tables II and III in the respective limits.

The results for finite $t$ and $U$ are shown in Table IV and Figs. 1–5. Table IV, columns 4 and 5, gives the symmetry of the exact ground state for $U>0$ and $U<0$, respectively. Column 4 is to be compared with the predictions of Hund's rules, column 3. The figures show the excitation energy of various states from the ground state for repulsive interactions (left-hand-side diagrams) and for attractive interactions (right-hand-side diagrams). The energies, in units of $4t+|U|$, are plotted as a function of the parameter $[U/(4t+|U|)]$. At the center of the figures we find noninteracting limit $U=0$ (Table II), and at either edge the extreme atomic limits $t=0$ (Table III).

The results are very rich in structure and information,

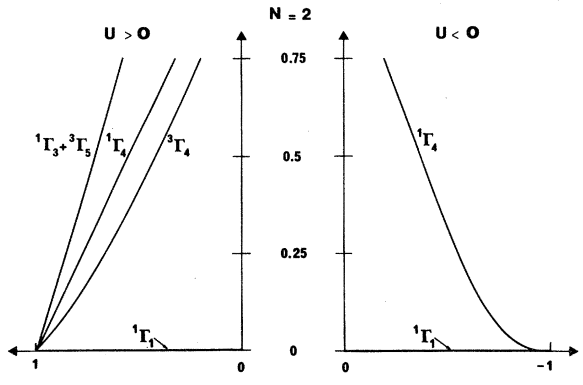


FIG. 1. Energies, as measured from the ground state, for $N=2$. The left-hand-side diagram corresponds to repulsive interactions $U>0$; the right-hand-side diagram corresponds to attractive interactions $U<0$. The abscissas correspond to the quantity $U/(4t+|U|)$. The ordinates are the excitation energies from the ground state in units of $4t+|U|$. The symmetries of ground and excited states are indicated.

TABLE V. Energy equations for the 56 eigenvalues.

| | | |
|---|---|---|
| $N=0$ | $^1\Gamma_1$ | $E=0$ |
| $N=1$ | $^2\Gamma_1$ | $E+3t=0$ |
| | $^2\Gamma_4$ | $E-t=0$ |
| $N=2$ | $^1\Gamma_1$ | $E^2+(4t-U)E-(12t^2+4tU)=0$ |
| | $^1\Gamma_3$ | $E-2t=0$ |
| | $^1\Gamma_4$ | $E^2-UE-4t^2=0$ |
| | $^3\Gamma_4$ | $E+2t=0$ |
| | $^3\Gamma_5$ | $E-2t=0$ |
| $N=3$ | $^2\Gamma_1$ | $E+t-U=0$ |
| | $^2\Gamma_3$ | $E^2-(2t+U)E-3t^2=0$ |
| | $^2\Gamma_4$ | $E^3+(3t-2U)E^2-(13t^2+5tU-U^2)E$ $-(15t^3-9t^2U-2tU^2)=0$ |
| | $^2\Gamma_5$ | $E^2-(2t+U)E-(3t^2-2tU)=0$ |
| | $^4\Gamma_2$ | $E-3t=0$ |
| | $^4\Gamma_5$ | $E+t=0$ |
| $N=4$ | $^1\Gamma_1$ | $E^2-3UE-(16t^2-2U^2)=0$ |
| | $^1\Gamma_3$ | $E^3-3UE^2-(16t^2-2U^2)E+24t^2U=0$ |
| | $^1\Gamma_4$ | $E^3-4UE^2-(16t^2-5U^2)E+(24t^2U-2U^3)=0$ |
| | $^1\Gamma_5$ | $E-U=0$ |
| | $^3\Gamma_2$ | $E-U=0$ |
| | $^3\Gamma_3$ | $E-U=0$ |
| | $^3\Gamma_4$ | $E-U=0$ |
| | $^3\Gamma_5$ | $E^3-2UE-(16t^2-U^2)E+8t^2U=0$ |
| | $^5\Gamma_2$ | $E=0$ |
| $N=5$ | $^2\Gamma_1$ | $E-t-2U=0$ |
| | $^2\Gamma_3$ | $E^2+(2t-3U)E-(3t^2+2tU-2U^2)=0$ |
| | $^2\Gamma_4$ | $E^3-(3t+5U)E^2-(13t^2-11tU-8U^2)E$ $+(15t^3+22t^2U-10tU^2-4U^3)=0$ |
| | $^2\Gamma_5$ | $E^2+(2t-3U)E-(3t^2+4tU-2U^2)=0$ |
| | $^4\Gamma_2$ | $E+3t-U=0$ |
| | $^4\Gamma_5$ | $E-t-U=0$ |
| $N=6$ | $^1\Gamma_1$ | $E^2-(4t+5U)E-(12t^2-12tU-6U^2)=0$ |
| | $^1\Gamma_3$ | $E+2t-2U=0$ |
| | $^1\Gamma_4$ | $E^2-5UE-(4t^2-6U^2)=0$ |
| | $^3\Gamma_4$ | $E-2t-2U=0$ |
| | $^3\Gamma_5$ | $E+2t-2U=0$ |
| $N=7$ | $^2\Gamma_1$ | $E-3t-3U=0$ |
| | $^2\Gamma_4$ | $E+t-3U=0$ |
| $N=8$ | $^1\Gamma_1$ | $E-4U=0$ |

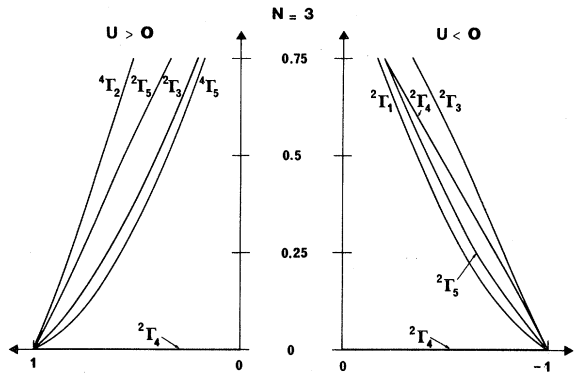


FIG. 2. Energies, as measured from the ground state, for $N=3$. See caption of Fig. 1.

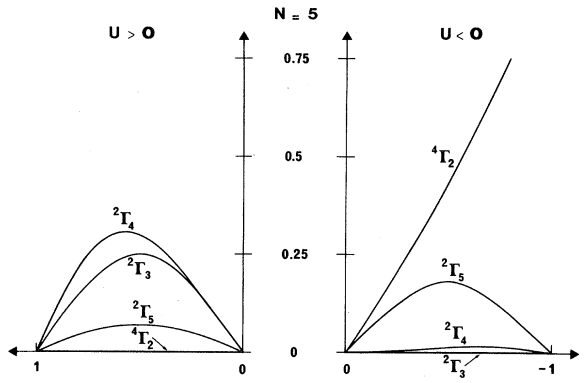


FIG. 4. Energies, as measured from the ground state, for $N=5$. See caption of Fig. 1.

and exhibit several surprising features, in addition to many expected results.

(A) The attractive-interaction cases all give ground states of expected minimum spin multiplicity.

(B) For repulsive interactions, Hund's rule works for $N=0$, 1, 2, 3, 5, 7, and 8. For $N=4$ the rule is violated (the ground state is a singlet $^1\Gamma_3$ instead of a triplet $^3\Gamma_5$). For $N=6$ the predicted $^3\Gamma_5$ is the ground state, but it is degenerate with a singlet $^1\Gamma_3$.

(C) At least for a small system with four centers, Hubbard's model allows, for some occupations, magnetic ground states (the $N=5$ and 6 cases). This feature seems to be a consequence of the degeneracy of the $p$-like one-electron orbital.

(D) In one instance ($N=6$, $U>0$) the ground state is "accidentally" degenerate, with a singlet and a triplet "sticking together" for any value of the parameters.

(E) For $N=4$, 5, and 6 there are very-low-lying excited states of other symmetries for any value of $U$. This effect is very pronounced in the $N=4$, $U>0$ case (compare with $N=6$, $U>0$) and especially in the $N=5$, $U<0$ case.

(F) As $U$ changes sign there are ground-state symmetry crossovers for $N=4$, 5, and 6, but not for the other occupancies. These crossovers involve changes in the space or in the space and spin symmetries.

(G) If the face-centered-cubic lattice is divided into four interpenetrating simple-cubic sublattices, and restriction is imposed that each atom in each sublattice is *identical* to each other atom in the same sublattice, a Hamiltonian identical to an infinite replica of (1.1) results. This can also be expressed as saying that (1.1) is the Hamiltonian of a face-centered-cubic lattice in which the wave functions are restricted to have the symmetries of the one $\Gamma$ and the three $X$ points of the Brillouin zone (i.e., a face-centered-cubic-lattice Hubbard Hamiltonian with Brillouin-zone sampling restricted to $\Gamma$ and $X$). Under these conditions—which are not as farfetched as they initially seem to be—a half-filled band with a repulsive $U$ would produce[14] a correlated ground state of full translational symmetry ($\Gamma$ point of the Brillouin zone), doubly degenerate and with no net spin. An occupation of $1.25e$/atom with a repulsive $U$ would produce a ferromagnetic state.

In conclusion, we find that our simple four-center Hubbard model, with two spin states per site and an arbitrary number of electrons, exhibits in the ground states a complexity of structure which defies easy generalizations.

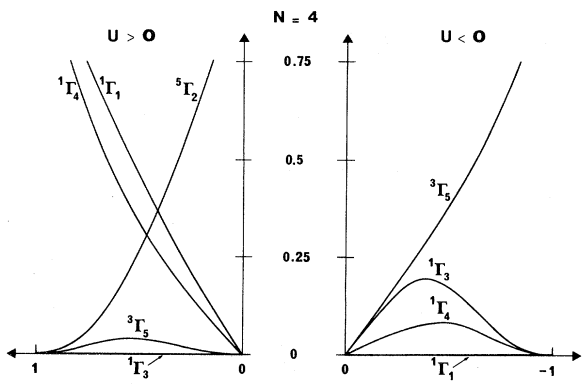


FIG. 3. Energies, as measured from the ground state, for $N=4$. See caption of Fig. 1.

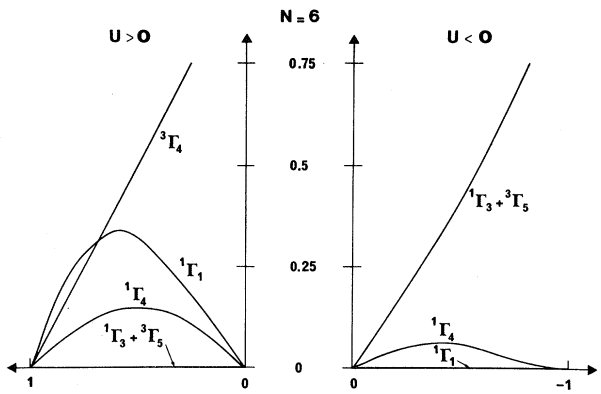


FIG. 5. Energies, as measured from the ground state, for $N=6$. See caption of Fig. 1.

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[14]Under the conditions of a face-centered-cubic lattice with restricted $\Gamma$ and $X$ sampling, there is a correspondence between the point-group symmetries of $T_d$ in the cluster and the space-group symmetry of the cubic lattice with $\Gamma_1$, $\Gamma_2$, and $\Gamma_3$ of $T_d$ corresponding to the $\Gamma$ point of the Brillouin zone, and $\Gamma_4$ and $\Gamma_5$ of $T_d$ corresponding to the $X$ point.