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► **To cite this version:**

Thomas Perez, Patrick Cassam-Chenaï. Generalization of the concepts of seniority number and ionicity. 2017. hal-01493163v2

HAL Id: hal-01493163

<https://hal.science/hal-01493163v2>

Preprint submitted on 19 Jun 2017 (v2), last revised 19 Sep 2017 (v3)

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Generalization of the concepts of seniority number and ionicity

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Abstract

We present here generalized versions of the concepts of seniority number and ionicity. Hermitian operators whose eigenspaces correspond to wave functions of definite seniority or ionicity values are introduced. The generalized seniority numbers (GSNs) afford to establish refined hierarchies of configuration interaction (CI) spaces within those of fixed ordinary seniority. The usefulness of such a hierarchy is illustrated on the buckminsterfullerene C_{60} molecule.

1 Introduction

The concept of seniority originates from the work of Racah on electrons in an atom¹. Since then, it has become very popular in nuclear physics^{2,3}. Its (re-)introduction in quantum chemistry by Bytautas et al.⁴ has proved very fruitful and has inspired many recent works (see⁸⁻¹¹ to quote a few). It is closely related to the notion of ionicity that has been used in valence-bond (VB) theory since the sixties⁷. Sometimes, it is used in some algorithms without actually being named^{5,6}.

Seniority affords to partition the n -electron Hilbert space into subspaces spanned by sets of Slater determinants having a definite number of unpaired orbitals. For closed-shell systems, it has been observed that the Full Configuration Interaction (FCI) energy is dominated by the contribution of the seniority-zero part of the wave function, when delocalized molecular orbitals are used, and that, the higher the seniority number of the determinants, the less important their contribution on average⁴. The situation is reversed in VB calculations⁹.

However, even if one restricts a CI space to a subspace of a given seniority number, the size of the CI can be prohibitively large. Therefore, it is of interest to push the seniority number partitioning strategy a step further, that is to say, to create other such numbers to further break down the seniority-zero subspace into a hierarchy of smaller subspaces. The purpose of this paper is to present a method describing the generalized seniority numbers with an illustration to the π -electron system of the buckminsterfullerene C_{60} molecule.

Our definition is based on the concepts put forward in Chapter 4 of the Ph. D thesis of M. Vivier, entitled *“Sur quelques théorèmes d’algèbre extérieure”*¹², and on their generalization to the case where the shells are not all of the same even dimension. As we shall

see, the usual seniority numbers appear in the particular case of primitive shells, hence the term “generalized seniority” we have coined for the general case. Our generalization is different from that of Talmi in nuclear structure theory¹³, where the partitioning is still in terms of pairs of particles, but where the form of the pairing functions goes beyond the simple Slater determinantal one.

The paper is organized as follows. In the first section, the concepts of generalized seniority number (GSN) and generalized ionicity (GI) are defined and explained. Then, we highlight interesting mathematical results relevant to this concept. Finally, we clarify its possible use on the C_{60} example and conclude.

2 Generalized seniority number and generalized ionicity

We consider a one-particle Hilbert space V which is the direct sum (not necessarily orthogonal) of n vector subspaces V_1, \dots, V_n of respective dimensions $2d_1, \dots, 2d_n$. Each of these subspaces will be called a “shell”, and the set $\{V_1, \dots, V_n\}$ a “shell partition”. In quantum chemistry, the V_i ’s can be the vector spaces spanned by sets of spin-orbital pairs corresponding to the same atomic orbital. In such a case, the shells will be termed tentatively “primitive shells”, as all the d_i ’s are equal to 1. Even with this restriction, there will be infinitely many possible shell partitions, as soon as $n > 1$. A natural shell partition with larger values for some d_i ’s occurs when the system has degenerate orbitals. If the sets of degenerate orbitals in increasing energy order are d_1 -, \dots , d_n -fold degenerate, then, the shells V_i ’s can be defined as the $2d_i$ -dimensional vector spaces spanned by the associated degenerate pairs of spin-orbitals.

We denote by u_i the single determinantal function built from a set of $2d_i$ normalized spin-orbitals, $(\chi_{i,1}, \dots, \chi_{i,2d_i})_{i=1, \dots, n}$ spanning the shell V_i :

$$\forall i \in \{1, \dots, n\}, \quad u_i = \chi_{i,1} \wedge \dots \wedge \chi_{i,2d_i} \quad , \quad (1)$$

where \wedge is the Grassmann (or exterior) product (which is intrinsically antisymmetrical)^{14,15}. Note that choosing a different set of linearly independent spin-orbitals would only change u_i by a constant factor.

Remark 1: In quantum chemistry, as mentioned above, the even dimension $2d_i$ of the V_i 's would arise from the fact that there are as many basis spin-orbitals of spin $+\frac{1}{2}$, as there are of opposite spin. However, in the following, to alleviate notation, we will not distinguish the spin of the spin-orbitals. In other words, the spin-orbitals will be labelled by indices running from 1 to $2d_i$, irrespective of their spin.

The symbol $(\chi)_1$ will designate the concatenated bases of the n shells,

$$(\chi)_1 := (\chi_{1,1}, \dots, \chi_{1,2d_1}, \chi_{2,1}, \dots, \chi_{2,2d_2}, \dots, \chi_{n,1}, \dots, \chi_{n,2d_n}) \quad , \quad (2)$$

which is a basis of the one-particle Hilbert space V . We will further denote by $(\chi)_N$ the N -particle basis set of Slater determinants induced by $(\chi)_1$

$$(\chi)_N := (\chi_{i_1, j_1} \wedge \dots \wedge \chi_{i_N, j_N})_{(i_1, j_1) < \dots < (i_N, j_N)} \quad , \quad (3)$$

where the order on the ordered pairs is the lexicographic order: $(i, j) < (k, l)$ if $i < k$ or if $i = k$ and $j < l$. The union of all these basis sets, $(\chi) := \bigcup_i (\chi)_i$, including $(\chi)_0 := (1)$, is a basis of the first quantization equivalent of the Fock space.

In second quantization, the $(\chi_{i,1}, \dots, \chi_{i,2d_i})$'s are created by the operators $a_{i,1}^\dagger, \dots, a_{i,2d_i}^\dagger$,

respectively, acting on the empty state $|0\rangle$:

$$a_{i,j}^\dagger|0\rangle = |\chi_{i,j}\rangle \quad , \quad (4)$$

so that,

$$a_{i,1}^\dagger \cdots a_{i,2d_i}^\dagger|0\rangle = |\chi_{i,1} \wedge \cdots \wedge \chi_{i,2d_i}\rangle = |u_i\rangle \quad . \quad (5)$$

Since the basis (χ) is not orthogonal, the corresponding annihilation operators $a_{i,j}$'s, defined by conjugation from Eq (4): $\langle 0|a_{i,j} = \langle \chi_{i,j}|$ are not very convenient, because $\langle 0|a_{i,j}a_{k,l}^\dagger|0\rangle = \langle \chi_{i,j}|\chi_{k,l}\rangle \neq \delta_{(i,j),(k,l)}$. In consequence, we introduce the dual basis $(\tilde{\chi})$, that is the unique basis verifying the following property:

$$\forall i, j, k, l, \quad \langle \tilde{\chi}_{i,j}|\chi_{k,l}\rangle = \delta_{(i,j),(k,l)} \quad , \quad (6)$$

where $\delta_{(i,j),(k,l)}$ is the Krönecker symbol for the ordered pair indices (i, j) and (k, l) . The corresponding annihilation operators, denoted by a tilde, that is to say: $\langle \tilde{\chi}_{i,j}| = \langle 0|\tilde{a}_{i,j}$, satisfy the desired relationship:

$$\langle 0|\tilde{a}_{i,j}a_{k,l}^\dagger|0\rangle = \delta_{(i,j),(k,l)} \quad . \quad (7)$$

It is also convenient to extend the notion of creation and annihilation operators to arbitrary quantum states. So, we denote the creation operator, $a^\dagger(f)$, of a general state,

$f = \sum_{(i_1,j_1),\dots,(i_k,j_k)} c_{(i_1,j_1),\dots,(i_k,j_k)} \chi_{i_1,j_1} \wedge \cdots \wedge \chi_{i_k,j_k}$, $c_{(i_1,j_1),\dots,(i_k,j_k)} \in \mathbb{C}$, as follows:

$$a^\dagger(f)|0\rangle = |f\rangle = \sum_{(i_1,j_1),\dots,(i_k,j_k)} c_{(i_1,j_1),\dots,(i_k,j_k)} a_{i_1,j_1}^\dagger \cdots a_{i_k,j_k}^\dagger|0\rangle \quad . \quad (8)$$

For example, $a^\dagger(\chi_{i,j}) = a_{i,j}^\dagger$ and $a^\dagger(u_i) = a_{i,1}^\dagger \cdots a_{i,2d_i}^\dagger$.

We define the “dual” annihilation operator of a product state, $\tilde{a}(u_i)$, as the product of

the dual annihilation operators, $\tilde{a}(\chi_{i,j}) = \tilde{a}_{i,j}$, in reverse order: $\tilde{a}(u_i) = \tilde{a}_{i,2d_i} \cdots \tilde{a}_{i,1}$, and more generally, by anti-linearity, the “dual” annihilation operator of $a^\dagger(f)$ as

$$\tilde{a}(f) = \sum_{(i_1,j_1),\dots,(i_k,j_k)} \bar{c}_{(i_1,j_1),\dots,(i_k,j_k)} \tilde{a}_{i_k,j_k} \cdots \tilde{a}_{i_1,j_1} \quad , \quad (9)$$

where the bar \bar{c} denotes complex conjugation.

Definition 1: We say that a $(2d_i - k)$ -particle Slater determinant x **is included in** u_i if there exists a set $\{h_1, \dots, h_k\}$ such that $a^\dagger(u_i) = a_{i,h_1}^\dagger \cdots a_{i,h_k}^\dagger a^\dagger(x)$.

So, for every Slater determinant $m \in (\chi)_N$ of the N -particle induced basis set, we can write:

$$a^\dagger(m) = a^\dagger(u_{i_1}) \cdots a^\dagger(u_{i_\omega}) a^\dagger(x_{j_1}) \cdots a^\dagger(x_{j_\Omega}) \quad , \quad (10)$$

where the x_{j_k} ’s are strictly included in some u_{j_k} ’s which are distinct from one another and from $u_{i_1}, \dots, u_{i_\omega}$.

Definition 2: We call ω the **generalized ionicity of m in the u_i ’s**. It represents the number of fully occupied shells.

Note that it is called the *degree of m in the u_i ’s* in mathematics¹². When the shells are chosen to be a set of primitive shells, ω is the ionicity number of the Slater determinant m , as defined in⁷ in the context of VB wave functions.

Definition 3: The integer Ω is called the **generalized seniority number of m relative to the u_i ’s**. It represents the number of non-empty, non-fully occupied shells.

Note that, when the shells are chosen to be a set of primitive shells, Ω is nothing but the seniority number of the Slater determinant m .

Remark 2: The integer $p = 2\omega + \Omega$ is called the **reduced degree of m** . It coincides with the number of particles of the Slater determinant in the primitive shell case i.e.

when $d_1 = \dots = d_n = 1$ (since, in this case, the u_i 's are 2-particle states and the x_j 's are necessarily 1-particle states).

The vector space spanned by all the Slater determinants, m , of the same GSN Ω is noted $M(\Omega)$. It only depends upon the shell partition and not upon the choice of the shell basis sets. By extension, all wave functions in subspace $M(\Omega)$ will be said of GSN Ω . The subset of $M(\Omega)$ containing the wave functions spanned by Slater determinants m of the same degree q in the u_i 's is a subvector space of $M(\Omega)$, noted $M(\omega, \Omega)$ with $\omega \in \{0, \dots, n - \Omega\}$. For a given Ω , $M(\Omega)$ is the direct sum of all the $M(\omega, \Omega)$'s. The $M(\omega, \Omega)$'s can be further decomposed into their projections onto the N -particle Hilbert spaces, noted $M(N, \omega, \Omega)$. In the next section, we will introduce a GSN operator, which acts diagonally on the $M(\Omega)$'s and whose expectation value on a normalized element of each $M(\Omega)$ is its GSN.

3 Hermitian operators related to the GSN and GI concepts

Definition 4: For $i \in \{1, \dots, n\}$ and any quantum state F , we consider the decomposition:

$$a^\dagger(F) = \hat{Q}_i(F) + \hat{R}_i(F) \quad , \quad (11)$$

where $\hat{Q}_i(F)$ represents the part of the $a^\dagger(F)$'s expansion in the (χ) -basis containing at least one $a^\dagger_{i,j}$, and $\hat{R}_i(F)$ the part of $a^\dagger(F)$ which does not contain any creation operator of a basis spin-orbital appearing in u_i . We call it the **residue** or the **rest of F relatively to u_i in the basis (χ)** .

$\hat{R}_i(F)$ can be expressed as

$$\hat{R}_i(F) = \tilde{a}(u_i)a^\dagger(u_i)a^\dagger(F) \quad , \quad (12)$$

and $\hat{Q}_i(F)$ can be further decomposed as

$$\hat{Q}_i(F) = \mathring{Q}_i(F) + a^\dagger(u_i)\tilde{a}(u_i)a^\dagger(F) \quad , \quad (13)$$

where $\mathring{Q}_i(F)$ represents the part of the $a^\dagger(F)$'s expansion containing at least one $a_{i,j}^\dagger$ but not $a^\dagger(u_i)$ entirely.

By combining Eqs. (11), (12) and (13), we obtain,

$$\mathring{Q}_i(F) = \left(1 - \tilde{a}(u_i)a^\dagger(u_i) - a^\dagger(u_i)\tilde{a}(u_i)\right)a^\dagger(F). \quad (14)$$

Remark 3: More generally, we can define $\mathring{Q}_{i_1, i_2, \dots, i_k}(F) = \mathring{Q}_{i_1}\mathring{Q}_{i_2} \cdots \mathring{Q}_{i_k}(F)$, (where the order of the i_j 's is indifferent since the \mathring{Q}_{i_j} 's commute), which extracts the part of the $a^\dagger(F)$'s expansion containing at least one a_{i_1, j_1}^\dagger , one a_{i_2, j_2}^\dagger , ... and one a_{i_k, j_k}^\dagger , without containing entirely $a^\dagger(u_{i_1})$ nor $a^\dagger(u_{i_2})$ nor ... nor $a^\dagger(u_{i_k})$.

Definition 5: The linear operator $\hat{\Omega} : G \mapsto \hat{\Omega}(G) := \sum_{i=1}^n \mathring{Q}_i(G)$ is called the **generalized seniority number operator**. It acts diagonally on any element of $M(\Omega)$:

$$\forall G \in M(\Omega), \quad \hat{\Omega}(G) = \Omega a^\dagger(G) \quad . \quad (15)$$

To prove the latter identity, let $G \in M(\Omega)$. The creation operator $a^\dagger(G)$ can be regarded as a linear combination of $a^\dagger(m)$'s, with $m \in (\chi)$ the induced basis of Slater determinants. For all m , we can write $a^\dagger(m) = a^\dagger(u_{i_1}) \cdots a^\dagger(u_{i_\omega}) a^\dagger(x_{j_1}) \cdots a^\dagger(x_{j_\Omega})$ (for some ω -value) with $a^\dagger(x_{j_1}) \cdots a^\dagger(x_{j_\Omega})|0\rangle \in M(0, \Omega)$. Applying $\hat{\Omega}$ to m and using Eq.

(14), the only non zero contributions come from $\mathring{Q}_{j_1}(m) = a^\dagger(m), \dots, \mathring{Q}_{j_\Omega}(m) = a^\dagger(m)$, respectively. So, we find exactly Ω times $a^\dagger(m)$ in $\hat{\Omega}(m)$. This being true for all the $a^\dagger(m)$'s appearing in the expression of $a^\dagger(G)$, by linearity of $\hat{\Omega}$, we obtain the identity, Eq. (15).

Similarly, a generalized ionicity operator can be defined as follows:

Definition 6: *The linear operator $\hat{\omega} : G \mapsto \hat{\omega}(G) = \sum_{i=1}^n a^\dagger(u_i)\tilde{a}(u_i)a^\dagger(G)$ is called the **generalized ionicity operator for the shell partition** $\{V_1, \dots, V_n\}$. It does not depend upon a change of basis of V_i , for any i . It acts diagonally on any element of the $M(\omega, \Omega)$'s:*

$$\forall G \in M(\omega, \Omega), \quad \hat{\omega}(G) = \omega a^\dagger(G) \quad . \quad (16)$$

To prove the latter identity, let $G \in M(\omega, \Omega)$. Applying $\hat{\omega}$ to an $m \in (\chi)$ in the expansion of G , whose creation operator can necessarily be cast in the form given in Eq. (10), the only contributing terms are $a^\dagger(u_{i_1})\tilde{a}(u_{i_1})a^\dagger(m) = a^\dagger(m), \dots, a^\dagger(u_{i_\omega})\tilde{a}(u_{i_\omega})a^\dagger(m) = a^\dagger(m)$, as $a^\dagger(u_i)\tilde{a}(u_i)a^\dagger(m) = 0$, for all $i \notin \{i_1, \dots, i_\omega\}$. So, $a^\dagger(m)$ appears exactly ω times in $\hat{\omega}(m)$. This being true for all the $a^\dagger(m)$'s appearing in the expression of $a^\dagger(G)$, by linearity of $\hat{\omega}$, we obtain the identity, Eq. (16).

Remark 4: A third identity follows from the previous two Eqs. (15) and (16),

$$\forall G \in M(\omega, \Omega), \quad (n - \omega - \Omega) a^\dagger(G) = \sum_{i=1}^n \hat{R}_i(G) \quad , \quad (17)$$

where the integer $(n - \omega - \Omega)$ is the number of empty shells in G .

Indeed, let $G \in M(\omega, \Omega)$. By using Eqs. (11) and (13), we can decompose $a^\dagger(G)$ in n different manners as follows:

$$\forall i \in \{1, \dots, n\}, \quad a^\dagger(G) = \mathring{Q}_i(G) + a^\dagger(u_i)\tilde{a}(u_i)a^\dagger(G) + \hat{R}_i(G) \quad . \quad (18)$$

By summing these n equalities and using Eqs. (15) and (16), we obtain:

$$n a^\dagger(G) = \Omega a^\dagger(G) + \omega a^\dagger(G) + \sum_{i=1}^n \hat{R}_i(G) \quad , \quad (19)$$

hence the result, Eq. (17).

The operator $\hat{\Omega}$ can be used to decompose the creation operator of an arbitrary quantum state F onto the vector spaces of definite GSN, the $M(\Omega)$'s. This can be achieved by using Löwdin projectors¹⁶, for example. Let $a^\dagger(F) = \sum_{\Omega=0}^n a^\dagger(G_\Omega)$, where $G_\Omega \in M(\Omega)$. From Eq. (15), we deduce,

$$\hat{\Omega}(F) = \sum_{\Omega=0}^n \Omega a^\dagger(G_\Omega) \quad . \quad (20)$$

For all $\Omega \neq 0$, we can extract the $\Omega a^\dagger(G_\Omega)$ component of this decomposition by projection,

$$\Omega a^\dagger(G_\Omega) = \prod_{\substack{0 \leq j \leq n \\ j \neq \Omega}} \frac{\hat{\Omega}(F) - j a^\dagger(F)}{\Omega - j} \quad . \quad (21)$$

Then, the generalized seniority-zero part of $a^\dagger(F)$ can be obtained by difference,

$$a^\dagger(G_0) = a^\dagger(F) - \sum_{\Omega \neq 0} a^\dagger(G_\Omega) = a^\dagger(F) - \sum_{\Omega \neq 0} \frac{1}{\Omega} \prod_{\substack{0 \leq j \leq n \\ j \neq \Omega}} \frac{\hat{\Omega}(F) - j a^\dagger(F)}{\Omega - j} \quad . \quad (22)$$

4 Application to the C_{60} Hückel energy levels

The primitive shell partition used to define seniority numbers in quantum chemistry stems from the fact that spin-orbitals of the same spin are degenerate with respect to spin symmetry for the spin-free Hamiltonian usually considered. It is therefore a

natural idea to take also into account spatial symmetry, that is to say, to partition the one-particle Hilbert space into subspaces closed with respect to both spin and spatial symmetry operation. The highest known finite group spatial symmetry in molecular system is the icosahedral symmetry. So, our generalization of the seniority number concept is well-illustrated by the study of the buckminsterfullerene C_{60} molecule.

It is our take that generalized seniority numbers based on spatial symmetry can be relevant parameters to limit CI expansions, as already observed for seniority number. This hypothesis relies on known phenomena, where a correlation has been established between the complete filling of a shell of a certain type and an unusual stability property. We have in mind the octet rule, the 18-electron rule or aromaticity, for example. So, we are going to investigate the convergence of CI calculations with respect to fine-tuned variational space hierarchies based on such GSNs.

Since our goal is just to establish a proof-of-principle, and not to aim at high accuracy prediction, we begin our study at the Hückel level of theory. As shown in Fig. 1, the one-particle Hilbert space is spanned by 60 orbitals, so $\dim V = 120$. If it is partitionned into the corresponding 60 primitive shells, we obtain the usual seniority numbers. However, even if one limits the CI space to seniority-zero Slater determinants, the latter will be of dimension $\binom{60}{30} \approx 1.18 \times 10^{17}$, which is clearly untractable. So, to further decompose the seniority-zero space, we are going to use GSNs associated to the shells corresponding to the degenerate orbitals displayed in Fig. 1.

More precisely, the shell partition consists of 15 shells, $V_1, V_2, V_3, \dots, V_{14}, V_{15}$ of dimensions 2, 6, 8, \dots , 8, 6, respectively. The largest shell V_6 is of dimension 18. The dimension of the GSN ($\Omega = 0$)-subspace of the seniority-zero space is 1464. For $\Omega \leq 1$, there are 601594 additional Slater determinants to include, and for $\Omega \leq 2$, another 53141130 Slater determinant set. All of these restricted CI subspaces are amenable to quantum chemistry computations in contrast with the full seniority-zero space. It remains to be verified that the Ω -based hierarchy is physically meaningful.

In order to assess convergence in a non-trivial case example, we need to add a two-electron term to the one-electron Hückel Hamiltonian used to obtain the eigenvectors corresponding to the levels of Fig. 1. We choose to add a term of the form given in the general seniority-zero Hamiltonian^{10,11}. Our total Hamiltonian can be expressed as:

$$\hat{H} = \sum_{p=1}^{60} (2h_{pp} + V_{pppp}) S_p^\dagger S_p + \sum_{1 \leq p < q \leq 60} (4V_{ppqq} - 2V_{ppq}) S_p^\dagger S_p S_q^\dagger S_q + \sum_{1 \leq p \neq q \leq 60} V_{ppqq} S_p^\dagger S_q \quad , \quad (23)$$

where h_{pp} is the p^{th} -eigenvalue of the Hückel matrix and where the quantity V_{pqrs} is an interelectronic repulsion integral:

$$V_{pqrs} = \sum_{i,j,k,l} c_{pi} c_{qj} c_{rk} c_{sl} \int_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{p_i^z(\vec{r}_1) p_j^z(\vec{r}_1) p_k^z(\vec{r}_2) p_l^z(\vec{r}_2)}{\|\vec{r}_1 - \vec{r}_2\|} d\vec{r}_1 d\vec{r}_2 \quad . \quad (24)$$

The c_{ij} 's are the coefficients of the Hückel eigenvector matrix and p_i^z is the STO-3G¹⁷ p_z -orbital centered on the i -th carbon atom.

5 Conclusion

The concepts of GSN and GI, generalizing those of seniority number and ionicity, have been introduced with their associated operators. The generalization is based on the partitioning of the one-particle Hilbert space into shells. From the mathematical point of view, the choice of the partition can be arbitrary. However, in practice, the partition should be chosen on physical ground.

In this paper, a partition of the spin-orbital basis functions according to their spatial and spin degeneracy has been considered. A hierarchy of CI-spaces based on the corresponding GSN has been proposed. The usefulness of this new hierarchy has been illustrated on C_{60} . The associated GSN affords to split the seniority-zero space of C_{60} for a basis set of 60 Hückel molecular orbitals into CI-subspaces of reduced dimensions, lending

themselves to numerical computations for low values of the GSN.

Acknowledgements

This work was supported by the grant CARMA ANR-12-BS01-0017.

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Figures

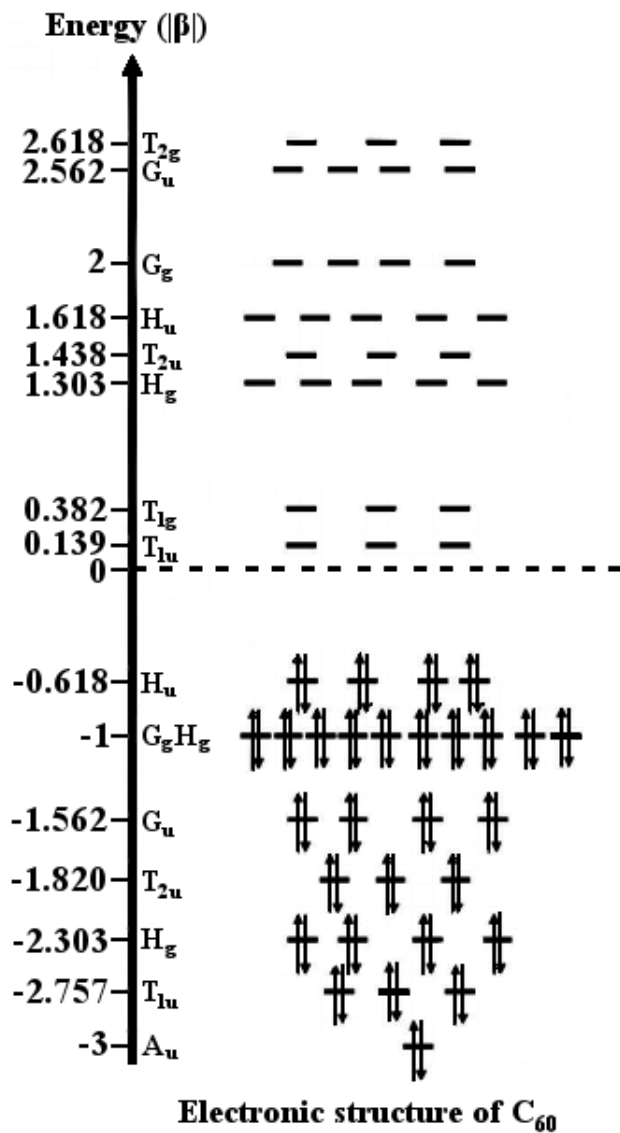


Figure 1: Energy diagram of C₆₀ Hückel molecular orbitals with electron occupation in the ground state reference configuration.