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Freeon unitary group formulation of Hartree–Fock theory

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Summary. Hartree–Fock theory was a major topic in Professor Löwdin's famous 1955 *Physical Review* papers. His development was based on fermion orbitals and the Slater determinant. Since that time there has been developed, at the University of Texas, the freeon, unitary-group formulation of quantum chemistry as a viable alternative to the fermionic formulations of nonrelativistic quantum chemistry. We wish to express our appreciation to Professor Löwdin for his strong support of our freeon studies and for many helpful conversations.

Key words: Hartree–Fock theory – Freeon unitary group formulation

1. Introduction

Nonrelativistic quantum chemistry is conventionally formulated in either the Slater determinant or the second-quantized formulations [1–10]. Both formulations employ the spin orbital, even though the Hamiltonian is independent of spin. This redundancy led the Texas group in the early 60s to formulate the *freeon symmetric group formulation* (FSGF) [11, 12] based on the symmetric group, S_N where N is the number of electrons. A decade later we reformulated the problem as the *freeon, unitary-group formulation* (FUGF) [13, 14] based on the unitary group $U(M)$, where M is the number of freeon orbitals. More recently we have applied FUGF to the nucleus where the freeon orbital is independent of the isospin orbital, and to baryons where the freeon orbital is independent of the color orbital.

FUGF has a number of useful features:

i) It exposes the basic dynamics of the problem which are hidden in a fermion formulation.

ii) It does not require spin projection.

iii) It focuses *de novo* on the orbital rather than the particle. In fact, particle indices do not appear in FUGF.

iv) It provides a facile evaluation of matrix elements.

v) It employs a simple operator algebra which is ideally suited to the development of Hartree–Fock, superoperator and other theories.

Section 2 contains a brief introduction to the symmetric group, its Frobenius algebra, the partition-labeling of freeon N-electron states and FSGF. Section 3 contains a brief introduction to the unitary group and its Lie algebra and FUGF and Sect. 4 contains the freeon theory. Section 5 contains the FUGF of Hartree–Fock theory for closed-shell and open-shell reference states. Note that since the theory is a freeon theory the resulting theory is the *restricted* Hartree–Fock theory (RHF). We illustrate this theory by means of the Hückel–Hubbard Hamiltonian, which contains as a variable parameter:

$$-1 \leqslant x \equiv U/(t+|U|) \leqslant 1 \tag{1}$$

where U is the repulsion energy of two electrons on a single site and t is the hopping integral (Hückel β) representing the covalent bonding between two sites.

2. The symmetric group and its Frobenius algebra

2.1 Introduction

The *symmetric group*, S_N, plays a major role in the theory of systems containing N identical particles. The group and its (Frobenius) algebra are introduced in Sect. 2.2. In Sect. 2.3 we construct its irreducible spaces from spaces which are invariant under S_N and its algebra. In Sect. 2.4 we discuss the permutational symmetry of the Hamiltonian of a system of N identical particles. In Sect. 2.5 the tensor product space is introduced as an approximation to the full Hilbert space of the N-particle Schrödinger Hamiltonian, which is then decomposed into S_N-irreducible spaces. In Sect. 2.6 we compute the matrix representation of the Hamiltonian in the S_N-irreducible spaces.

2.2 The group and its Frobenius algebra

The symmetric group [12] is denoted:

$$S_N = \{\boldsymbol{P}_i, i = 1 \text{ to } N!\} \tag{2}$$

where N is a positive integer. It has a simple rule of multiplication:

$$\boldsymbol{P}_i \boldsymbol{P}_j = g_{ij}^k \boldsymbol{P}_j \tag{3}$$

where $g_{ij}^k = 0$ or 1. The *Frobenius algebra* of S_N is an operator vector space denoted:

$$FA(S_N) : \{\boldsymbol{P}_i, i = 1 \text{ to } N!\} \tag{4}$$

An equivalent basis is the *Wigner basis*:

$$FA(S_N) : \{\boldsymbol{e}_{rs}^{[\lambda]}, r, s = 1 \text{ to } f[\lambda], [\lambda] \text{ ranging}\} \tag{5}$$

where

$$\boldsymbol{e}_{rs}^{[\lambda]} = (f[\lambda]/N) \sum_{i=1}^{N!} [P_i^{-1}]_{sr}^{[\lambda]} \boldsymbol{P}_i \tag{6}$$

and $[P_i^{-1}]_{sr}^{[\lambda]}$ is the element of the s^{th} row, r^{th} column in the matrix representing P^{-1} in the irreducible rrepresentation labeled by $[\lambda]$:

$$[\lambda] = [\lambda_1, \ldots \lambda_k, \ldots \lambda_M], \quad \lambda_1 \geqslant \lambda_k \geqslant \cdots \geqslant 0 \tag{7}$$

with the constraint:

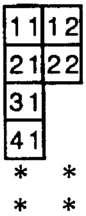
$$\sum_{k=1}^{M} \lambda_k = N \tag{8}$$

is a *partition* of N. A partition is graphically represented by a *Young diagram*, $YD[\lambda]$, an array of N squares with λ_i squares in the i^{th} row.

We denote the dimension of the $[\lambda]^{\text{th}}$ irreducible representation denoted by $f[\lambda]$ and computed by:

$$f[\lambda] = \frac{N!}{\prod hD[\lambda]} \tag{9}$$

where $\prod hD[\lambda]$ is the product of integers in the *hook diagram* for the selected Young diagram:



and where $\boxed{ij}$ is a *hook length*, the number of squares traversed by an arrow drawn from the right through the i^{th} row and hooking down the j^{th} column. For $N = 3$ we have three partitions and three irreducible spaces. See Table 1.

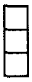
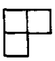
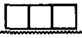
The Wigner elements of the S_N-Frobenius algebra multiply according to:

$$e_{rs}^{[\lambda]} e_{tu}^{[\lambda']} = \delta([\lambda], [\lambda'])\delta(s, t)e_{ru}^{[\lambda]} \tag{10}$$

The Frobenius contains a subalgebra, the *centrum* whose elements commute with every element in the full algebra. The centrum is spanned by *projectors*:

$$FA(S_N)_C\{e^{[\lambda]}\} \tag{11}$$

Table 1. The dimensions of the S_N-irreducible representations for $N = 3$

[λ]	YD[λ]	f[λ]
$[1^3]$		$6/\begin{array}{\|c\|}\hline 3\\\hline 2\\\hline 1\\\hline\end{array} = 6/6 = 1$
$[2.1]$		$6/\begin{array}{\|c\|c\|}\hline 3 & 1\\\hline 1 & \\\cline{1-1}\end{array} = 6/3 = 2$
$[3]$		$6/\begin{array}{\|c\|c\|c\|}\hline 3 & 2 & 1\\\hline\end{array} = 6/6 = 1$

where

$$\boldsymbol{e}^{[\lambda]} = \sum_{r=1}^{f[\lambda]} \boldsymbol{e}_{rr}^{[\lambda]} \tag{12}$$

so that

$$\boldsymbol{e}^{[\lambda]}\boldsymbol{e}^{[\lambda']} = \delta([\lambda], [\lambda'])\boldsymbol{e}^{[\lambda]} \tag{13}$$

and

$$[\boldsymbol{P}, \boldsymbol{e}^{[\lambda]}] = 0, \quad \text{for every } \boldsymbol{P} \text{ and } \boldsymbol{e}^{[\lambda]} \tag{14}$$

The identity permutation is the sum of the projectors (the resolution of the identity):

$$\boldsymbol{I} = \sum_{[\lambda]} \boldsymbol{e}^{[\lambda]} \tag{15}$$

2.3 The irreducible representation spaces

We take $\mathscr{V}$ as a space which is invariant under S_N; i.e.,

$$\boldsymbol{P}\mathscr{V} = \mathscr{V} \tag{16}$$

An important example of a space $\mathscr{V}$ with this property is the tensor product space of Sect. 2.5. By the resolution of the identity we can decompose $\mathscr{V}$ as follows:

$$\begin{aligned} \mathscr{V} &= \boldsymbol{I}\mathscr{V} \\ &= \sum_{[\lambda]} \boldsymbol{e}^{[\lambda]}\mathscr{V} \\ &= \sum_{[\lambda]} \mathscr{V}^{[\lambda]} \end{aligned} \tag{17}$$

where

$$\mathscr{V}^{[\lambda]} = \boldsymbol{e}^{[\lambda]}\mathscr{V} \tag{18}$$

is an *irreducible representation space* of S_N. Note that it is invariant under S_N; i.e.:

$$\begin{aligned} \boldsymbol{P}\mathscr{V}^{[\lambda]} &= \boldsymbol{P}\boldsymbol{e}^{[\lambda]}\mathscr{V} \\ &= \boldsymbol{e}^{[\lambda]}\boldsymbol{P}\mathscr{V} \\ &= \boldsymbol{e}^{[\lambda]}\mathscr{V} \\ &= \mathscr{V}^{[\lambda]} \end{aligned} \tag{19}$$

$\mathscr{V}^{[\lambda]}$ is in turn decomposed into components i.e.:

$$\boldsymbol{e}^{[\lambda]} = \sum_{r=1}^{f[\lambda]} \boldsymbol{e}_{rr}^{[\lambda]} \tag{20}$$

Hence

$$\begin{aligned} \mathscr{V}^{[\lambda]} &= \sum_{r=1}^{f[\lambda]} \boldsymbol{e}_{rr}^{[\lambda]}\mathscr{V} \\ &= \sum_{r=1}^{f[\lambda]} \mathscr{V}_{r}^{[\lambda]} \end{aligned} \tag{21}$$

where

$$\mathcal{V}_r^{[\lambda]} = \boldsymbol{e}_{rr}^{[\lambda]}\mathcal{V} \tag{22}$$

Since V is a representation space of S_N we have:

$$\mathcal{V}_r^{[\lambda]} = \boldsymbol{e}_{r1}^{[\lambda]}\mathcal{V}_1^{[\lambda]} \tag{23}$$

More specifically let $|[\lambda]1i\rangle$ be the i^{th} orthonormal basis vector in $V_1^{[\lambda]}$. Then:

$$|[\lambda]ri\rangle = \boldsymbol{e}_{r1}^{[\lambda]}|[\lambda]1i\rangle \tag{24}$$

and for $\boldsymbol{P} \in S_N$:

$$\langle[\lambda]ri|\boldsymbol{P}|[\lambda']r'i'\rangle = \delta_{i,i'}\delta_{\lambda,\lambda'}[\boldsymbol{P}]_{rr'}^{[\lambda]} \tag{25}$$

2.4 The N-particle Hamiltonian

For a system containing N identical particles, there exists a N-particle, Schrödinger Hamiltonian, $\boldsymbol{H}_S$ such that:

$$[\boldsymbol{H}_S, \boldsymbol{P}] = 0, \quad \boldsymbol{P} \in S_N \tag{26}$$

where $\boldsymbol{P}$ is an element of S_N which permutes the indices on the N identical particles. It follows that the Hilbert space, V_H, of $\boldsymbol{H}$ is a representation space of S_N; i.e.:

$$\boldsymbol{P}\mathcal{V}_H = \mathcal{V}_H \tag{27}$$

which, as shown in Sect. 2.3, $\mathcal{V}$ can be decomposed into a direct sum of irreducible spaces,

$$\mathcal{V} = \sum_{[\lambda]} \sum_{r=1}^{f[\lambda]} \mathcal{V}_r^{[\lambda]} \tag{28}$$

The matrix elements of $\boldsymbol{H}$ on $\mathcal{V}$ are given by:

$$\begin{aligned}
\langle\mathcal{V}_r^{[\lambda]}|\boldsymbol{H}_S|\mathcal{V}_{r'}^{[\lambda']}\rangle &= \langle\mathcal{V}|\boldsymbol{e}_{1r}^{[\lambda]}\boldsymbol{H}_S\boldsymbol{e}_{r'1}^{[\lambda']}|\mathcal{V}\rangle \\
&\langle\mathcal{V}|\boldsymbol{H}_S\boldsymbol{e}_{1r}^{[\lambda]}\boldsymbol{e}_{r'1}^{[\lambda']}|\mathcal{V}\rangle \\
&= \delta([\lambda],[\lambda'])\delta(r,r')\langle\mathcal{V}|\boldsymbol{H}_S\boldsymbol{e}_{11}^{[\lambda]}|\mathcal{V}\rangle \\
&= \delta([\lambda],[\lambda'])\delta(r,r')\langle\mathcal{V}|\boldsymbol{H}_S\boldsymbol{e}_{11}^{[\lambda]}\boldsymbol{e}_{11}^{[\lambda]}|\mathcal{V}\rangle \\
&= \delta([\lambda],[\lambda'])\delta(r,r')\langle\mathcal{V}|\boldsymbol{e}_{11}^{[\lambda]}\boldsymbol{H}_S\boldsymbol{e}_{11}^{[\lambda]}|\mathcal{V}\rangle \\
&= \delta([\lambda],[\lambda'])\delta(r,r')\langle\mathcal{V}_1^{[\lambda]}|\boldsymbol{H}_S|\mathcal{V}_1^{[\lambda]}\rangle
\end{aligned}$$

It follows that representation of $\boldsymbol{H}_S$ on the Hilbert space is factored into blocks, which in turn are further factored into $f[\lambda]$ separate degenerate blocks, each labeled by $[\lambda]$ and the degeneracy index r, so that $[\lambda]$ and r are the S_N *quantum numbers.*

2.5 The tensor product space

Since the exact Hilbert space of the N-particle Hamiltonian is unknown, we approximate it by an N^{th} tensor-product space constructed from an M dimensional one-particle (orbital) space:

$$\mathcal{V}_M : \{|1\rangle, |2\rangle, \ldots |M\rangle\} \tag{30}$$

The N^{th} rank tensor-product space is denoted:

$$\mathscr{V}_M(N):\{|R(N)\rangle = |R_1\rangle|R_2\rangle|R_3\rangle\cdots|R_N\rangle, \dim = M^N\} \tag{31}$$

Each $R(N)$ characterized by a configuration (weight) denoted by:

$$\{w\} = \{w_1, w_2, \ldots, w_M\} \tag{32}$$

where $w_1, w_2, \ldots, w_M$ are the occupation numbers of $|1\rangle, |2\rangle, \ldots, |M\rangle$ in $R(N)$ and where:

$$\sum_{R=1}^{M} w_R = N \tag{33}$$

$\mathscr{V}_M(N)$ is invariant under S_N so that it can be decomposed into invariant spaces as described in Sect. 2.2:

$$\mathscr{V}_M|\lambda]:\{|[\lambda]\{w\}t\rangle t = 1 \text{ to } f_M[\lambda]\}$$

where t distinguishes among configuration states with the same $[\lambda]$ and $\{w\}$. The eigenvectors and eigenvalues are obtained by diagonalizing $\boldsymbol{H}_S$ in the several physical irreducible spaces and constitute a prediction of the spectrum.

3. The unitary group formulation

3.1 Introduction

In this section we replace $\boldsymbol{H}_S$ acting on $\mathscr{V}_M(M)$ by the equivalent unitary group Hamilton, $\boldsymbol{H}_U$ and compute its representation in the irreducible spaces of $U(M)$. The $U(M)$ quantum number is a partition of N, just as for S_N. In Sect. 3.2 we give a brief review of the theory of the unitary group and its Lie algebra; in Sect. 3.3 we construct $\boldsymbol{H}_U$.

3.2 The unitary group; its Lie and its covering algebras

The unitary group [15, 16, 17, 14], denoted:

$$U(M) = \{\boldsymbol{u}(\alpha), \text{ where } \alpha \text{ is a complex skew-Hermitian matrix parameterizing the group}\}$$

is the group isomorphic to the set of unitary transformations on an M-dimensional vector space. Its Lie algebra is denoted:

$$LAU(M):\{\boldsymbol{E}_{RS}, R, S = 1 \text{ to } M)\}$$

with Lie products:

$$[\boldsymbol{E}_{RS}, \boldsymbol{E}_{TU}] = \delta(S, T)\boldsymbol{E}_{RU} - \delta(R, U)\boldsymbol{E}_{TS} \tag{34}$$

The group elements are related to the Lie algebra elements via exponentiation. A general element of $U(M)$ may be written as:

$$\boldsymbol{u}(\alpha) = e^{\boldsymbol{Z}(\alpha)}$$

where $\boldsymbol{Z}(\alpha)$ is a skew-Hermitian element, i.e.:

$$\boldsymbol{Z}(\alpha)^\dagger = -\boldsymbol{Z}(\alpha)$$

hence

$$\boldsymbol{u}(\alpha)^{\dagger} = \boldsymbol{u}(\alpha)^{-1}$$

and specifically:

$$\boldsymbol{Z}(Z) = \sum_{R=1}^{M} \sum_{S=1}^{M} \alpha_{RS}\boldsymbol{E}_{RS} \quad \text{where } \alpha_{RS} = -\alpha_{SR}^{*} \tag{35}$$

Often a real parameterization of the group elements is useful, in that case we can take:

$$\boldsymbol{Z}(X, Y) = i\sum_{R=1}^{M} Y_{RR}\boldsymbol{E}_{RR} + \frac{i}{\sqrt{2}}\sum_{R=1}^{M}\sum_{S=1}^{R-1} Y_{RS}(\boldsymbol{E}_{RS} + \boldsymbol{E}_{SR}) + \frac{i}{\sqrt{2}}\sum_{R=1}^{M}\sum_{S=1}^{R-1} X_{RS}(\boldsymbol{E}_{RS} - \boldsymbol{E}_{SR}) \tag{36}$$

where the parameters X_{RS} and Y_{RS} are real. Note that $\alpha_{RS} = (X_{RS} + iY_{RS})/\sqrt{2}$ for $R > S$.

The *covering algebra* of $U(M)$ covers the operator space of the full unitary group and is spanned by the identity and all products of the generators; i.e.:

$$CAU(M): \{\boldsymbol{I}, \boldsymbol{E}_{RS}, \boldsymbol{E}_{RS}\boldsymbol{E}_{TU}, \ldots\} \tag{37}$$

The group elements $e^{\boldsymbol{Z}}$ are a subset of $CAU(M)$. The *centrum* of $CAU(M)$ is also a subset of $CAU(M)$ and is denoted:

$$CEU(M): \{\boldsymbol{C}_K K = 1 \text{ to } M\} \tag{38}$$

where $\boldsymbol{C}_K$ is a *Casimir opertor*, a K^{th} order polynomial in the generators such that:

$$[\boldsymbol{C}_K, \boldsymbol{E}_{RS}] = 0 \tag{39}$$

For example, the linear and quadratic Casimir operators are respectively:

$$\boldsymbol{C}_1 = \sum_{R=1}^{M} \boldsymbol{E}_{RR} \tag{40}$$

and

$$\boldsymbol{C}_2 = \sum_{R=1}^{M}\sum_{S=1}^{M} \boldsymbol{E}_{RS}\boldsymbol{E}_{SR} \tag{41}$$

The tensor product space, $\mathcal{V}_M(N)$ is invariant under $U(M)$ when we express its generators in terms of M^2 orbital ketbras; e.g.:

$$\boldsymbol{E}_{RS} = \sum_{j=1}^{N} |R_j\rangle\langle S_j| \tag{42}$$

The group elements represent an orbital transformation on the tensor product space. The enveloping algebra represents the set of excitations and de-excitations. The most general unitary orbital transformation on this space is given by Eq. (35) or equivalently Eq. (36). To demonstrate this we note:

$$\begin{aligned} \boldsymbol{Z} &= \sum_{R=1}^{M} \sum_{S=1}^{M} Z_{RS} \boldsymbol{E}_{RS} \\ &= \sum_{R=1}^{M} \sum_{S=1}^{M} \sum_{j=1}^{N} Z_{RS} |R_j\rangle\langle S_j| \\ &= \sum_{j=1}^{N} \sum_{R=1}^{M} \sum_{S=1}^{M} Z_{RS} |R_j\rangle\langle S_j| \end{aligned} \tag{43}$$

Employing $[|R_i\rangle\langle S_i|, |T_j\rangle\langle U_j|] = 0$ for $i \neq j$ we have:

$$e^{\boldsymbol{Z}} = \prod_{j=1}^{N} \exp\left(\sum_{R=1}^{M} \sum_{S=1}^{M} Z_{RS} |R_j\rangle\langle S_j| \right) \tag{44}$$

hence, each individual electron is transformed by the same unitary transformation. In other words, the unitary group elements represent the set of all possible unitary orbital transformations.

3.3 The irreducible spaces of U(M)

The irreducible spaces, denoted $\mathscr{V}^{\Gamma}$, of $U(M)$ are by Schur's lemma spaces which are diagonal for the mutually-commuting Casimir operators and are uniquely labeled by the eigenvalues of the Casimir operators:

$$\Gamma = \{C_K^{\Gamma} K = 1 \text{ to } M\} \tag{45}$$

For a basis of $\mathscr{V}_{\Gamma}$ we choose vectors which are diagonal in the *Cartan subalgebra* $\{\boldsymbol{E}_{RR} : R = 1 \text{ to } M\}$, the set of mutually-commuting, diagonal generators. The eigenvectors, called *weight vectors*, are denoted $|\Gamma[w]t\rangle$ where:

$$[w] = w_1, w_2, \ldots, w_M]$$

is called the *weight*. That is:

$$\boldsymbol{E}_{RR} |\Gamma[w]t\rangle = w_R |\Gamma[w]t\rangle \tag{46}$$

and

$$\boldsymbol{C}_K |\Gamma[w]t\rangle = C_K^{\Gamma} |\Gamma[w]t\rangle \tag{47}$$

where t distinguishes among weight vectors with the same weight.

The application of an off-diagonal generator $\boldsymbol{E}_{RS} R \neq S$, to a weight vector generates a new weight vector with a weight different from the weight of the original vector by integers. The highest-weight vector is a vector whose weight is such that:

$$w^{\Gamma} = [w_R^{\Gamma}], \qquad w_1^{\Gamma} \geqslant w_2^{\Gamma} \geqslant \cdots \geqslant w_M^{\Gamma} \geqslant 0 \tag{48}$$

and has property:

$$\boldsymbol{E}_{RS} |\Gamma[w]\rangle = 0 \quad \text{for } R < S \tag{49}$$

The highest weight vector is unique and so provides a label for the irreducible space V^{Γ}. For the tensor product basis of Sect. 2.5 with the choice of $\boldsymbol{E}_{RS}$ employed in Sect. 3.2 we have

$$\Gamma = [w^{\Gamma}] = [\lambda] \tag{50}$$

and

$$C_1^{\Gamma} = N = \sum_{R=1}^{M} w_R \tag{51}$$

The partition $[\lambda]$ acts as a label of both S_N and $U(M)$.

3.4 *The dimension of* $\mathcal{V}_M[\lambda]$

The dimension $f_M[\lambda]$ of $\mathcal{V}_M[\lambda]$ is given by the construction based on the Young diagram, $YD[\lambda]$:

$$f_M[\lambda] = \frac{\prod nD[\lambda]}{\prod hD[\lambda]} \tag{52}$$

Here, $\prod MD[\lambda]$ is the product of the integers in the *M-diagram*, $MD[\lambda]$:

$$\begin{array}{|c|c|} \hline M & M+1 \\ \hline M-1 & M \\ \hline M-2 & M-1 \\ \hline M-3 & \ldots \\ \hline \ldots & \\ \cline{1-1} \end{array} \tag{53}$$

and $\prod hD[\lambda]$ is the product of integers in the *hook diagram* discussed in Sect. 2. See Table 2.

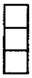
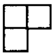
3.5 *The Gel'fand states and diagrams*

The invariant spaces, $\mathcal{V}_M[\lambda]$ of $U(M)$ are spanned by *Gel'fand states* which are weight-states, symmetry-adapted to the chain:

$$U(M) \supset U(M-1) \supset \cdots U(1) \tag{54}$$

These states are labeled by *Gel'fand diagrams* constructed by adding the orbital

Table 2. The dimensions, $f_M[\lambda]$ of the irreducible spaces for $N = M = 3$

[λ]	YD[λ]	f[λ]
$[1^3]$		$\begin{array}{\|c\|}\hline 3\\ \hline 2\\ \hline 1\\ \hline\end{array} / \begin{array}{\|c\|}\hline 3\\ \hline 2\\ \hline 1\\ \hline\end{array} = 6/6 = 1$
$[2,1]$		$\begin{array}{\|c\|c\|}\hline 3 & 4\\ \hline 2 \\ \cline{1-1}\end{array} / \begin{array}{\|c\|c\|}\hline 3 & 1\\ \hline 1 \\ \cline{1-1}\end{array} = 24/3 = 8$
$[3]$		$\begin{array}{\|c\|c\|c\|}\hline 3 & 4 & 5\\ \hline\end{array} / \begin{array}{\|c\|c\|c\|}\hline 3 & 2 & 1\\ \hline\end{array} = 60/6 = 10$

symbols in nondecreasing order along rows and increasing order down columns. As an example of $M = 3$ we denote the orbital space by:

$$\mathscr{V}_3 : \{|a\rangle, |b\rangle, |c\rangle\} \tag{55}$$

with orbital-labeling given by; i.e.:

$$a < b < c \tag{56}$$

See Table 3.

In the freeon formulation Sect. 4 the space $\mathscr{V}_3[3]$ is Pauli forbidden. However, in elementary particle theory the freeon orbitals $|a\rangle$, $|b\rangle$ and $|c\rangle$ are replaced by the flavor orbitals, $|u\rangle$ (up), $|d\rangle$ (down) and $|s\rangle$ strange, respectively. The, $\mathscr{V}_3[3]$ represents the baryon decuplet and $\mathscr{V}_3[2, 1]$ represents the baryon octet.

3.6 *The construction of Gel'fand states*

3.6.1 Introduction. To compute the matrix elements of the generators over the Gel'fand states we require an explicit algebraic construction of these states. In Sect. 3.6.2 we introduce an intermediate basis, the *generator basis* [18], formed by the application of weight-lowering generators to the unique highest-weight state. The generator basis is overcomplete and nonorthonormal. In Sect. 3.6.3 we give an example of the construction of the orthonormal Gel'fand states from generator states by the Moshinsky–Nagel procedure [19].

3.6.2 The generator basis. The *generator basis* [18] of $V_M[\lambda]$ is composed of vectors generated by applying weight-lowering generators to the highest weight, state which is denoted $|0\rangle$; e.g.:

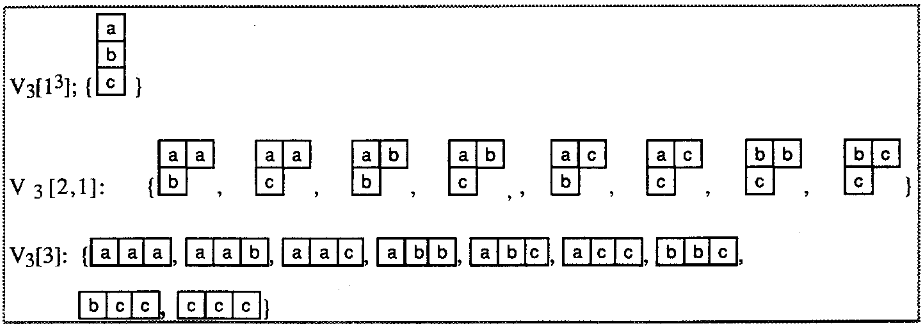
$$|\mathscr{G}) = |SR, UT, \ldots) = E_{SR}E_{UT} \cdots |0\rangle \tag{57}$$

Generator states with different weights are orthogonal since:

$$(\mathscr{G}|E_{RR}|\mathscr{G}') = w_R\{\mathscr{G}|\mathscr{G}') = \{\mathscr{G}|\mathscr{G}')w'_R \tag{58}$$

Hence, $\{\mathscr{G}|\mathscr{G}') = 0$ for $\{w'\} \neq \{w'\}$.

Table 3. Gel'fand diagrams for $N = M = 3$



The simplest complete set of generator states for $V_3[2, 1]$ and $V_3:\{|a\rangle, |b\rangle, |c\rangle\}$ are listed below:

$$V_3[2, 1]:\left\{|0\rangle = \begin{array}{|c|c|}\hline a & a \\ \hline b & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array},\ |ba),\ |ca),\ |cb),\ |baca),\ |bacb),\ |caca),\ |cacb)\right\} \tag{59}$$

The normalization of generator states is carried out by means of the Lie products of the generators. For example:

$$\begin{aligned}(ca \mid ca) &= \langle 0|E_{ac}E_{ca}|0\rangle \\ &= \langle 0|(E_{ca}E_{ac} + E_{aa} - E_{cc})|0\rangle \\ &= \langle 0|(0+2-0)|0\rangle = 2\end{aligned} \tag{60}$$

since $|0\rangle$ contains a two times and c zero times. So:

$$|ac\rangle = |ac)/\sqrt{2} \tag{61}$$

Similarly:

$$(bacb \mid bacb) = 1 \tag{62}$$

Note that these two equal-weight states are not orthogonal; e.g.:

$$(ca \mid bacb) = -1 \tag{63}$$

3.6.3 The Moshinsky–Nagel construction. The Moshinsky–Nagel [19] construction is based on weight-lowering polynomials, denoted $\boldsymbol{G}$ such that a Gel'fand state is given by:

$$\begin{aligned}|G\rangle &= N_G\boldsymbol{G}|0\rangle \\ &= \Sigma_{\mathscr{G}} C_{G,\mathscr{G}}|\mathscr{G})\end{aligned} \tag{64}$$

where the coefficients $G_{G,\mathscr{G}}$ are determined by the Moshinsky–Nagel construction. The inverse transformation is given by:

$$\begin{aligned}|\mathscr{G}\rangle &= N_G\boldsymbol{G}|0\rangle \\ &= \Sigma_G|G\rangle\langle G|\mathscr{G})\end{aligned} \tag{65}$$

The Moshinsky–Nagel construction has been computer-programmed by the authors. In addition, quite efficient bases [20–24] and construction methods exist for two column Gel'fand states. In Table 4 we list the Gel'fand states expressed as generator states for $M = N = 3$.

3.6.4 Freeon tensor product states. The direct product of two single column LAU(μ) Gel'fand bases forms a representation space of LAU(μ). The direct product states we denote as freeon tensor product states (FTP states) [24]. These states are the same as the Clifford algebra states of Paldus and coworkers [21, 22].

Since FTP states are the tensor product of two orthonormal states the FTP states are orthonormal. For example:

$$<\begin{array}{|c|}\hline a \\ \hline e \\ \hline f \\ \hline\end{array} \otimes \begin{array}{|c|}\hline c \\ \hline d \\ \hline\end{array} \Big| \begin{array}{|c|}\hline a \\ \hline c \\ \hline e \\ \hline\end{array} \otimes \begin{array}{|c|}\hline d \\ \hline f \\ \hline\end{array}> = <\begin{array}{|c|}\hline a \\ \hline e \\ \hline f \\ \hline\end{array} \Big| \begin{array}{|c|}\hline a \\ \hline c \\ \hline e \\ \hline\end{array}><\begin{array}{|c|}\hline c \\ \hline d \\ \hline\end{array} \Big| \begin{array}{|c|}\hline d \\ \hline f \\ \hline\end{array}> = 0\bullet 0 = 0$$

$$<\begin{array}{|c|}\hline a \\ \hline e \\ \hline f \\ \hline\end{array} \otimes \begin{array}{|c|}\hline c \\ \hline d \\ \hline\end{array} \Big| \begin{array}{|c|}\hline a \\ \hline e \\ \hline f \\ \hline\end{array} \otimes \begin{array}{|c|}\hline c \\ \hline d \\ \hline\end{array}> = <\begin{array}{|c|}\hline a \\ \hline e \\ \hline f \\ \hline\end{array} \Big| \begin{array}{|c|}\hline a \\ \hline e \\ \hline f \\ \hline\end{array}><\begin{array}{|c|}\hline c \\ \hline d \\ \hline\end{array} \Big| \begin{array}{|c|}\hline c \\ \hline d \\ \hline\end{array}> = 1\bullet 1 = 1$$

Table 4. Gel'fand states for $V_3[2, 1]$

$\begin{array}{|c|c|}\hline a & a \\ \hline b & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} = |0\rangle$

$\begin{array}{|c|c|}\hline a & a \\ \hline c & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} = |cb)$

$\begin{array}{|c|c|}\hline a & b \\ \hline b & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} = |ba)$

$\begin{array}{|c|c|}\hline a & b \\ \hline c & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} = |bacb)/\sqrt{2}$

$\begin{array}{|c|c|}\hline a & c \\ \hline b & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} = (2|ca) + |bacb)/\sqrt{6}$

$\begin{array}{|c|c|}\hline a & c \\ \hline c & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} = |cacb)$

$\begin{array}{|c|c|}\hline b & b \\ \hline c & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} = - |baca)$

$\begin{array}{|c|c|}\hline b & c \\ \hline c & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} = - |caca)/2$

Matrix elements may be evaluated efficiently and simply on the FTP basis. The Gel'fand basis vectors may be converted to and from the FTP basis through a fast transformation procedure [24].

3.7 The unitary group Hamiltonian

3.7.1 Introdution. There exists a unitary-group Hamiltonian of the form:

$$H_U = \sum_{RS} h_{RS} E_{RS} + (1/2) \sum_{RSTU} V_{RSTU}(E_{RS}E_{TU} - \delta(S, T)E_{RU}) \qquad (66)$$

which reproduces the representation of H_S on $V_M(N)$. Here, h_{RS} is the parameter for the one-particle interaction and V_{RSTU} is a parameter for the two-particle interaction. The total number of parameters is $M^2 + M^4$ but they are interrelated by the requirements of hermiticity as well as time-reversal, inversion and $R(3) - SU(2)$ symmetries. The parameters comprise the total information content of H_U. The diagonalization of H_U in the appropriated irreducible spaces of $U(M)$ constitutes a prediction of the spectrum.

4. Freeon theory

4.1 Introduction

In the tensor-product approximation the fermion orbital is taken to be the product of two orbitals: an energetically-inert spin orbital, denoted $|S\rangle$, and a freeon orbital, denoted $|R\rangle$, is free of spin. Fermion theory has the inherent weakness that it weights equally both the freeon and the spin orbitals and obscures the freeon dynamics. In its place we employ the *freeon theory* [13, 14] which exhibits more clearly the freeon dynamics and simplifies the theory since spin projection is not required.

To develop the freeon theory we return to the theory of the symmetric group. It is convenient to employ different conventions for the freeon Wigner operators than the spin N-particles. The freeon Wigner operators acting on freeon orbitals are defined conventionally as:

$$\boldsymbol{e}_{rs}^{[\lambda_R]} = \frac{\chi_1^{[\lambda_\nu]}}{N!} \sum_P \boldsymbol{P}^\nu [\boldsymbol{P}]_{sr}^{[\lambda_R]*} \tag{67}$$

and the spin Wigner operators acting only on the spin orbitals as:

$$\widetilde{\boldsymbol{e}_{rs}^{[\lambda_R]}} = \frac{\chi_1^{[\lambda_\sigma]}}{N!} \sum_P (-1)^{\Pi(P)} \boldsymbol{P}^\sigma [\boldsymbol{P}]_{sr}^{[\lambda_R]} \tag{68}$$

The choice used in Eq. (68) is valid since the complex conjugate of a set of irreducible representation matrices gives a set of irreducible representation matrices (possibly equivalent or inequivalent) and the parity term $(-1)^{\Pi(P)}$ is conserved in the multiplication of permutations.

We construct a complete set of projected freeon and spin N-particle states using the Wigner operators:

$$|\lambda_R R(N) t\rangle \propto \boldsymbol{e}_{t1}^{[\lambda_R]} |R(N)\rangle \tag{69}$$

and

$$|\tilde{\lambda}_{\mathscr{R}} S(N) u\rangle \propto \widetilde{\boldsymbol{e}_{u1}^{[\lambda_{\mathscr{R}}]}} |S(N)\rangle \tag{70}$$

respectively.

Next we apply the antisymmetric projector which we first expand in terms of Wigner operators as:

$$\boldsymbol{e}^{[1^N]} = \sum_{[\lambda]} \frac{1}{\chi_1^{[\lambda]}} \sum_{r,s} \boldsymbol{e}_{rs}^{[\lambda]} \otimes \widetilde{\boldsymbol{e}_{rs}^{[\lambda]}} \tag{71}$$

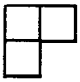
$$\begin{aligned} &\boldsymbol{e}^{[1^N]} |\lambda_R R(N) t\rangle \otimes \tilde{\lambda}_{\mathscr{R}} S(N) u\rangle \\ &\quad = \sum_{[\lambda]} \frac{1}{\chi_1^{[\lambda]}} \sum_{r,s} (\boldsymbol{e}_{rs}^{[\lambda]} |\lambda_R R(N) t\rangle) \otimes (\widetilde{\boldsymbol{e}_{rs}^{[\lambda]}} |\tilde{\lambda}_{\mathscr{R}} S(N) u\rangle) \qquad (72) \\ &\quad = \delta(t, u) \delta(\lambda_R, \lambda_{\mathscr{R}}) \frac{1}{\chi_1^{[\lambda_R]}} \sum_r |\lambda_R R(N) r\rangle \otimes |\tilde{\lambda}_R (S(N)) r\rangle \qquad (73) \end{aligned}$$

Therefore the complete set of antisymmetric states have form:

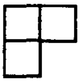
$$|[1^N] R^{[\lambda_R]} \mathscr{R}^{[\tilde{\lambda}]_R}\rangle = \frac{1}{\sqrt{\chi_1^{[\lambda_R]}}} \sum_r |\lambda_R R(N) r\rangle \otimes |\tilde{\lambda}_R S(N) r\rangle \tag{74}$$

The conjugate representation is graphically equivalent to a representation where the number and lengths of the rows in $[\lambda_R]$ is equal to the number and lengths of the columns in the conjugate representation, $[\tilde{\lambda}_R]$, e.g.:

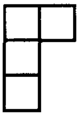
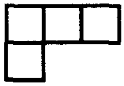
is conjugate to



is conjugate to



(i.e., self-conjugate)

 is conjugate to 

For the important case where we have a "spin" formed out of two orbitals only, we have:

$$YD[S] = [N - S, S] \tag{75}$$

where N is the number of particles and S is the spin. Consequently, $YD[R]$ has form:

$$YD[R] = [W^{N/2-S}, 1^{2S}] \tag{76}$$

The *spin quantum number* of the N-particle state is a consequence of this conjugacy:

$$S = (L_1 - L_2)/2$$

where $L_1 \geqslant L_2 \geqslant 0$ are the lengths of the two columns of the Gel'fand state such that $N = L_1 + L_2$.

Let $\boldsymbol{H}_F$ be any operator commuting with the set of permutations and with the following property:

$$\boldsymbol{H}_F(|R(N)\rangle \otimes |S(N)\rangle) = (\boldsymbol{H}'_F|R(N)\rangle) \otimes |S(N)\rangle \tag{77}$$

Then,

$$\begin{aligned}&\langle [1^N]R'^{[\lambda_R]}\mathscr{R}^{[\widetilde{\lambda}_R]}|\boldsymbol{H}_F|[1^N]R^{[\lambda_R]}\mathscr{R}^{[\widetilde{\lambda}_R]}\rangle \\ &\quad = \delta(R, R')\delta(\lambda_R, \lambda'_R)\langle \lambda'_R R'(N)1|\boldsymbol{H}'_F|\lambda_R(N)1\rangle\end{aligned} \tag{78}$$

This is the basis of the freeon theory where $[\widetilde{\lambda}_R]$ supplies the familiar spin label. The freeon, unitary-group formulation has been extensively and widely applied in the theory of light-atom molecules and their reactions.

4.2 *The Hückel–Hubbard Hamiltonian*

We use the Hückel–Hubbard Hamiltonian, $\boldsymbol{H}_H$ as a pedagogical device to illustrate many of the principles of FUGF. The Hückel–Hubbard Hamiltonian can be expressed in terms of site orbitals or molecular orbitals.

4.2.1 *The site-orbital representation*

$$\boldsymbol{H}_H = (|x| - 1)\sum_{\langle rs\rangle}(\boldsymbol{E}_{rs} + \boldsymbol{E}_{sr}) + x\boldsymbol{d} \tag{79}$$

where $\langle rs\rangle$ denotes nearest neighbors and:

$$\boldsymbol{d} = \sum_{r=1}^{M}(\boldsymbol{E}_{rr}^2 - \boldsymbol{E}_{rr}) \tag{80}$$

is the operator that counts the number of doubly-occupied sites.

4.2.2 *The molecular orbital representation for the linear polyenes*

$$\begin{aligned}\boldsymbol{H}_H = {} & (|x| - 1)\sum_{k=1}^{M} 2\cos\left(\frac{\pi k}{M+1}\right)E_{kk} \\ & + \tfrac{1}{2}\sum_{k_1=1}^{M}\sum_{k_2=1}^{M}\sum_{k_3=1}^{M}\sum_{k_4=1}^{M} V_{k_1,k_2,k_3,k_4}(\boldsymbol{E}_{k_1,k_2}\boldsymbol{E}_{k_3,k_4} - \delta(k_2, k_3)\boldsymbol{E}_{k_1k_4})\end{aligned} \tag{81}$$

where

$$\begin{aligned}V_{k_1,k_2,k_3,k_4} = \left(\frac{x}{2M+2}\right)&(\gamma(k_1+k_2+k_3+k_4) - \gamma(k_1+k_2+k_3-k_4)\\ &- \gamma(k_1+k_2+k_3+k_4) + \gamma(k_1+k_2-k_3-k_4)\\ &- \gamma(k_1-k_2+k_3+k_4) + \gamma(k_1-k_2+k_3+k_4)\\ &+ \gamma(k_1-k_2-k_3+k_4) - \gamma(k_1-k_2-k_3-k_4))\end{aligned}$$

and $\gamma(x) = \delta(0, x \text{ modulo } (2M+2))$.

The ethylene MO Hamiltonian is:

$$\begin{aligned}H_U = (|x|-1)(\mathbf{E}_{11} - \mathbf{E}_{22}) + \frac{x}{4}(&\mathbf{E}_{11}\mathbf{E}_{11} + \mathbf{E}_{22}\mathbf{E}_{22} + \mathbf{E}_{12}\mathbf{E}_{21}\\ &+ \mathbf{E}_{21}\mathbf{E}_{12} + \mathbf{E}_{12}\mathbf{E}_{12} + \mathbf{E}_{21}\mathbf{E}_{21} + \mathbf{E}_{11}\mathbf{E}_{22} + \mathbf{E}_{22}\mathbf{E}_{11} - 2\mathbf{E}_{11} - 2\mathbf{E}_{21})\end{aligned}$$

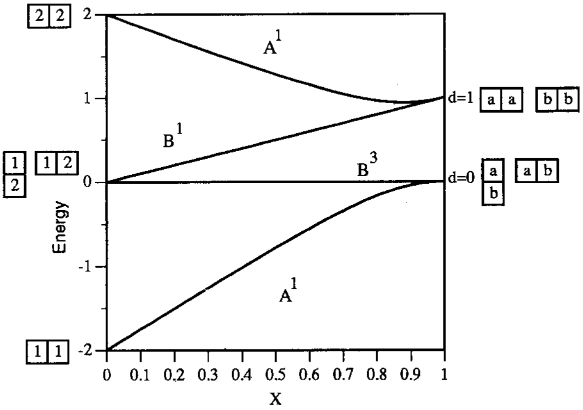


Fig. 1. The Hückel–Hubbard spectrum of ethylene

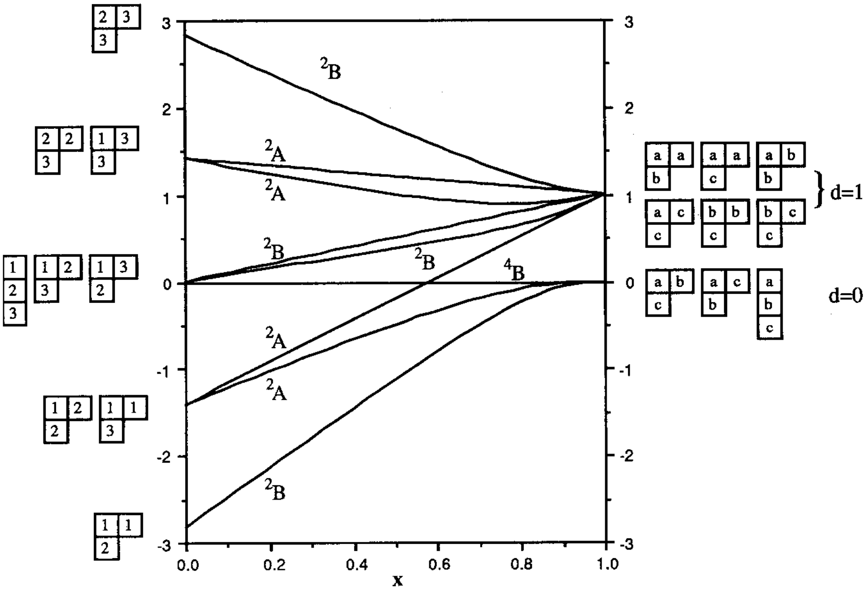


Fig. 2. The Hückel–Hubbard spectrum of the allyl radical.

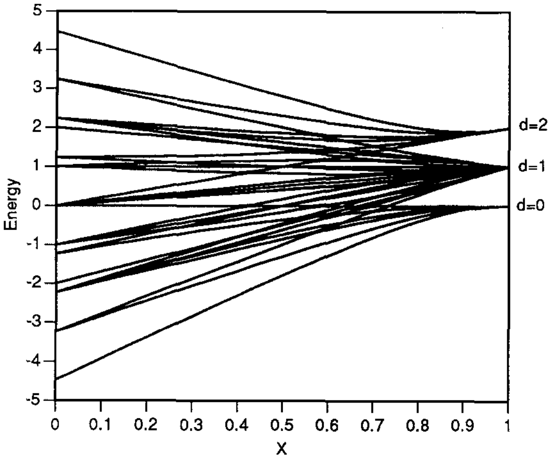


Fig. 3. The Hückel–Hubbard spectrum of butadiene

The Hückel–Hubbard spectra of ethylene, the allyl radical and linear butadience are shown in Figs. 1, 2, and 3, respectively.

5. The FUG formulation of Hartree–Fock theory

5.1 Introduction

The FUG single-configuration, HF theory varies freeon orbitals in the highest-weight state so as to minimize the ground state energy expectation value. This contrasts with the more usual Slater determinantal and second-quantized approaches [6, 8, 9]. The first spin free formulation of HF theory is due to Poshusta and Kramers [25] who employed the symmetric group. The formulation presented here is based on the unitary group formulation, much of which is based on earlier work done in collaboration with Dr. Connie Nelin. Since the theory is a freeon theory it is a *restricted HF* theory [26, 27]. We develop in the background theory in Sect. 5.3 and the open and closed shell theory in Sect. 5.3. We illustrate these theories with Hückel–Hubbard model of ethylene, the allyl radical and linear butadiene.

5.2 Basic formulation

5.2.1 Reference state and its orbital transformations. In the FUG formulation of HF theory we employ a trial state consisting of the highest weight state of $U(M)$. We then vary all orbitals within the M orbital space to minimize the ground state energy expectation value. Let $|0\rangle$ be an highest weight state of $U(M)$ with weight $\{w_1, w_2, w_3, \ldots, w_M\}$. The highest weight state has properties:

$$\langle 0|0\rangle = 1 \tag{82a}$$

$$E_{rr}|0\rangle = w_r|0\rangle \tag{82b}$$

$$\text{if } r \neq s \quad \text{and} \quad w_r \geqslant w_s \quad \text{then } E_{rs}|0\rangle = 0 \tag{82c}$$

The above three properties also characterize an extreme weight state (a Weyl reflection of the highest weight state). Hence the results that follow will hold for any extreme weight state as well.

We will now transform all orbitals within the M orbital space to minimize the ground state energy expectation value. We first show that we may restrict the transformation to be a unitary group element. Define $\boldsymbol{g}$ to have form:

$$\boldsymbol{g} = \sum_{r=1}^{M} \sum_{s=1}^{M} g_{rs} \boldsymbol{E}_{rs}$$

with no restriction on the complex numbers X_{rs}. Following the same techniques employed in Sect. 3.3 we have:

$$\exp(\boldsymbol{g}) = \prod_{i=1}^{N} \exp\left(\sum_{r=1}^{M} \sum_{s=1}^{M} g_{rs} |r_1\rangle\langle s_i| \right) \tag{83}$$

hence each individual electron is transformed by the same nonsingular transformation as required for an orbital transformation. Next consider $e^{\boldsymbol{g}}|0\rangle$, where $|0\rangle$ is a highest (extreme) weight state. This represents the most general trial vector of the desired form. Via Schur decomposition we can decompose $e^{\boldsymbol{g}}$ as:

$$e^{\boldsymbol{g}} = e^{-\boldsymbol{Z}} e^{\boldsymbol{L}} \tag{84}$$

where

$$\boldsymbol{Z} = \sum_{r=1}^{M} \sum_{s=1}^{M} Z_{rs} \boldsymbol{E}_{rs}, \qquad Z_{rs} = -Z_{sr}^{*} \tag{85}$$

and

$$\boldsymbol{L} = \sum_{r=1}^{M} \sum_{s=1}^{M} L_{rs} \boldsymbol{E}_{rs} \quad \text{and} \quad L_{rs} = 0 \quad \text{for } w_r > w_s. \tag{86}$$

Using the extreme weight property we have $e^{\boldsymbol{g}}|0\rangle = \exp(\sum_{r=1}^{M} L_{rr} w_r)\, e^{-\boldsymbol{Z}}|0\rangle$. The most general normalized trial vector therefore has form $e^{\boldsymbol{g}}|0\rangle$.

5.2.2 Extrenum conditions. We now proceed to the problem of minimizing the ground state expectation. The expectation value is given by $\langle 0|(e^{-\boldsymbol{Z}})^{\dagger} \boldsymbol{H} e^{-\boldsymbol{Z}}|0\rangle / \langle 0|(e^{-\boldsymbol{Z}})^{\dagger}\, e^{-\boldsymbol{Z}}|0\rangle$. Using unitarity this reduces to $\langle 0\, e^{\boldsymbol{Z}} \boldsymbol{H} e^{-\boldsymbol{Z}}|0\rangle$. The Baker–Campbell–Hausdorff formula gives:

$$\begin{aligned} e^{\boldsymbol{Z}} \boldsymbol{H} e^{-\boldsymbol{Z}} = \boldsymbol{H} &+ \frac{1}{1!}[\boldsymbol{Z}, \boldsymbol{H}] + \frac{1}{2!}[\boldsymbol{Z}, [\boldsymbol{Z}, \boldsymbol{H}]] + \frac{1}{3!}[\boldsymbol{Z}, [\boldsymbol{Z}, [\boldsymbol{Z}, \boldsymbol{H}]]] \\ &+ \frac{1}{4!}[\boldsymbol{Z}, [\boldsymbol{Z}, [\boldsymbol{Z}, [\boldsymbol{Z}, \boldsymbol{H}]]]] + \cdots \end{aligned} \tag{87}$$

We denote $\boldsymbol{Z}_F$ as any skew-Hermitian operator that is a local extrenum of $\langle 0|\, e^{\boldsymbol{Z}} \boldsymbol{H} e^{-\boldsymbol{Z}}|0\rangle$, hence we may make definition $|0_F\rangle = e^{-\boldsymbol{Z}_F}|0\rangle$. To be a local extrenum requires $\langle 0|\, e^{(\boldsymbol{Z}_F + z)} \boldsymbol{H} e^{-(\boldsymbol{Z}_F + z)}|0\rangle$ to be zero to first order in z, where z is of the same form as $\boldsymbol{Z}$. But $e^{(\boldsymbol{Z}_F + z)} = e^{\boldsymbol{Z}_F} e^{\boldsymbol{Z}'}$, where the group property gives $e^{-\boldsymbol{Z}_F} e^{(\boldsymbol{Z}_F + z)} = e^{\boldsymbol{Z}'}$ where $\boldsymbol{Z}'$ is of the same functional form as $\boldsymbol{Z}$. Therefore, the first order variation in $\langle 0|\, e^{(\boldsymbol{Z}_F + z)} \boldsymbol{H}\, \mathrm{e}^{-(\boldsymbol{Z}_F + z)}|0\rangle$ is of the form $\langle 0_F|\, e^{\boldsymbol{Z}'} \boldsymbol{H} e^{-\boldsymbol{Z}'}|0_F\rangle$. The extrenum condition is equivalent to requiring the first order variation of $\langle 0_F|\, e^{\boldsymbol{Z}'} \boldsymbol{H} e^{-\boldsymbol{Z}'}|0_F\rangle$ in $\boldsymbol{Z}'$ to be zero.

$$\langle 0_F|[\boldsymbol{Z}', \boldsymbol{H}]|0_F\rangle = 0 \tag{88}$$

for all generators $(\boldsymbol{Z}')$ of $U(M)$. We can employ basis vectors of $\boldsymbol{Z}'$ as $(\boldsymbol{E}_{rs} - \boldsymbol{E}_{sr})$

and $i(\boldsymbol{E}_{rs}+\boldsymbol{E}_{sr})$ with real coefficients. Hence, the extrenum condition is equivalent to $\langle 0_F|[\boldsymbol{E}_{rs}, \boldsymbol{H}]|0_F\rangle = 0$ for all r, s. When $\boldsymbol{E}_{rs}$ is an excitation (i.e. $w_r < w_s$) from $|0\rangle_{\mathrm{F}}$ this last equation reduces to $\langle 0_F|\boldsymbol{H}\boldsymbol{E}_{rs}|0_F\rangle = 0$ which is the *Brillion extrenum condition* for the Hartree–Fock ground state.

The vanishing of the first derivative of the variation function is an extrenum condition. We generally are interested not in extrenum but in minima. To determine if the extrenum is a likely candidate for being a local minima we ask if the second order variation in $\langle 0_n|\boldsymbol{H}|0_n\rangle$ is positive. To obtain the local minimization condition we employ the second order term in the Baker–Campbell–Hausdorff expansion and test for the condition:

$$\langle 0_n|[[\boldsymbol{Z}, [\boldsymbol{Z}, \boldsymbol{H}]]|0_n\rangle \geqslant 0 \quad \text{for all } \boldsymbol{Z} \text{ of the form above}$$

Since $\boldsymbol{Z}^{\dagger} = -\boldsymbol{Z}$, we have

$$\langle 0_n|[[\boldsymbol{Z}, [\boldsymbol{Z}, \boldsymbol{H}]]|0_n\rangle = \langle 0_n|[[\boldsymbol{Z}^{\dagger}, \boldsymbol{H}], \boldsymbol{Z}]|0_n\rangle = \langle 0_n|[\boldsymbol{Z}^{\dagger}, [\boldsymbol{H}, \boldsymbol{Z}]]|0_n\rangle$$

For this reason the symmetric commutator $([[\boldsymbol{Z}^{\dagger}, \boldsymbol{H}], \boldsymbol{Z}] + [\boldsymbol{Z}^{\dagger}, [\boldsymbol{H}, \boldsymbol{Z}]])/2 = [\boldsymbol{Z}^{\dagger}, \boldsymbol{H}, \boldsymbol{Z}]$ is normally employed in formulas for the second variations. The necessary matrix elements for computation of this quantity are given in Appendix B for the freeon highest (extreme) weight state. We also must note that it is possible that more than one local minima may exist in a problem, presumably we should take the Hartree–Fock state as the lowest energy state among these local minima.

The quantity $\langle 0|e^{\boldsymbol{Z}}\boldsymbol{H}e^{-\boldsymbol{Z}}|\mathbf{0}\rangle$ is highly nonlinear in the parameters Z_{rs}; hence, generally cannot be minimized in one analytic step. Many numerical approaches could be used i.e., steepest descent, conjugate gradients, etc. However, most methods employed in chemistry are based on linear approximations of the extrenum condition in the form of a fixed point iteration (self-consistency) or a Newton–Cotes procedure employing the explicit form of the second order variations mentioned above.

In any case, it is convenient to define a Fock operator $\boldsymbol{F}_n$ such that $\boldsymbol{F}_n^{\dagger} = \boldsymbol{F}_n$ and:

$$\boldsymbol{F}_n = \sum_{R=1}^{M} \sum_{S=1}^{M} F^n_{rs}\boldsymbol{E}_{rs} \tag{89}$$

which we require to have property:

$$\langle 0_n|[\boldsymbol{E}_{rs}, \boldsymbol{H}]|0_n\rangle = \langle 0_n|[\boldsymbol{E}_{rs}, \boldsymbol{F}_n]|0_n\rangle \tag{90}$$

In other words we require $\boldsymbol{F}_n$ to have the same first order variation in $\langle 0_n|\boldsymbol{F}_n|0_n\rangle$ as $\langle 0_n|\boldsymbol{H}|0_n\rangle$ does. The motivation for the form of Eq. (89) is that $\boldsymbol{F}_n$ may be exactly diagonalized by diagonalizing the $M \times M$ matrix with elements F^n_{rs}. It is important to note that there are actually fewer independent equations than unknowns F^n_{rs}. Specifically, for cases such that $w_r = w_s$ Eq. (90) gives $0 = 0$. As a result the terms F^n_{rs} for $w_r = w_s$ are *not* determined by the above equations [6]. In a group theoretical language the ground state is invariant under the direct product group, $U(M_0) \otimes U(M_1) \otimes U(M_2) \cdots \otimes U(M_2) \otimes \cdots$ where $U(M_w)$ denotes the set of unitary transformations within the set of orbitals with common weight w.

To give an alternate motivation for the definition of $\boldsymbol{F}$ we consider the vector $\boldsymbol{H}|0_n\rangle$. We wish to find an operator $\boldsymbol{F}_n$ of form of Eq. (89) and $\boldsymbol{F}_n^{\dagger} = \boldsymbol{F}_n$ such that the vector $(\boldsymbol{H} - \boldsymbol{F}_n)|0_n\rangle$ is as small as possible. Specifically, we minimize

$\langle 0_n|(H - F_n)^2|0_n\rangle$ over the possible values F^n_{rs}. The resulting extrenum conditions give $\langle 0_n|(H - F_n)|0_n\rangle = 0$, $\langle 0_n|[(H - F_n), E_{rs}]|0_n\rangle = 0$.

Therefore, the resulting Fock operator also minimizes the norm of the residual vector $(H - F_n)|0_n\rangle$, representing the "best" approximation to H for a given fixed orbital basis. It is therefore reasonable to assume that an eigenstate to F_n is an approximate eigenstate of H. Hence, we will be choosing new orbitals where F_n is (block) diagonal.

This gives the basis for the following classical algorithm originally presented by Roothaan [4, 5]. We compute the Hartree–Fock orbitals by the *self-consistent method* consisting of the following steps:

1. Choose a set of orbitals, $V:\{|r\rangle\}$.
2. Evaluate the coefficients in the Fock operator F.
3. Diagonalize F in the primary orbital basis to obtain a second orbital basis $\{|r'\rangle\}$.
4. Replace old orbitals $\{|r\rangle\}$. with new orbitals $\{|r'\rangle\}$.
5. Repeat steps 1 thru 4 until the Fock operator does not change; i.e., until they are self-consistent.

Since the Hartree–Fock theory is a variation theory the Hartree–Fock ground state energy is greater than or equal to the exact ground-state energy. The difference between the two:

$$E_c = E(HF) - E(CI)$$

is called the correlation energy or correlation error. The term correlation error is used since the Hartree–Fock theory is a mean-field theory.

5.3 FUG Hartree–Fock equations

To implement the extrenum conditions we will require the expectation values of the various operators, H, $[H, E_{rs}]$, F and $[F, E_{rs}]$. While there are many methods of evaluating these quantities, we will employ the simplest method applicable to an extreme weight state of $U(M)$.

5.3.1 Freeon Hartree Fock energy (ground state expectation value). For the typical two-body Hamiltonian we have:

$$H = H_0 + V$$

where

$$H_0 = \sum_{r=1}^{M} \sum_{s=1}^{M} h_{rs} E_{rs} \tag{91}$$

and

$$V = \tfrac{1}{2} \sum_{r=1}^{M} \sum_{s=1}^{M} \sum_{t=1}^{M} \sum_{u=1}^{M} V_{rstu} E_{rstu} \tag{92}$$

where the coefficients obey $h_{rs} = h^*_{sr}$, $V_{rstu} = V_{turs} = V^*_{utsr}$.

We combine Eqs. (128) and (135) of Appendix A to yield:

$$\langle 0|H|0\rangle = \sum_{r=1}^{M} w_r h_{rr} + \tfrac{1}{2} \sum_{r=1}^{M} \sum_{t=1}^{M} V_{rrtt} w_r w_t - \tfrac{1}{2} \sum_{r=1}^{M} \sum_{t=1}^{M} V_{rttr} \min(w_r, w_t) \tag{93}$$

5.3.2 Freeon Hartree orbital energies. Equation (93) was derived assuming that for each r, s that $w_r - w_s$ is an integer. Nevertheless, we can extend the equation to be defined over real values of weights w_r, which will allow us to (formally) differentiate the energy in respect to the weights w_r. The "physical" interpretation of such an operation is analogous to the operation of adding an infinitesimal charge at a position to measure the electric field, i.e., this represents the effective field seen by the orbital "r". Employing:

$$\frac{\partial \langle 0|\boldsymbol{H}|0\rangle}{\partial w_r} = h_{rr} + \sum_{t=1}^{M} V_{rrtt} w_t - \left(\sum_{w > w_r} \sum_{\substack{t \\ w_t = w}} V_{rttr} + \tfrac{1}{2} \sum_{\substack{t \\ w_t = w_r}} V_{rttr} \right) \tag{94}$$

We will later see that this choice is consistent with an orbital energy definition of the corresponding Hartree–Fock orbital.

5.3.3 Freeon Hartree–Fock operator. To find the appropriate Fock operator $\boldsymbol{F}_n$ we need to evaluate Eq. (90) for form of Eq. (89). We start by evaluating the required commutators. For *any p* and *h* we have:

$$\begin{aligned}
[\boldsymbol{E}_{ph}, \boldsymbol{H}_0] &= \left[\boldsymbol{E}_{ph}, \sum_{r=1}^{M} \sum_{s=1}^{M} h_{rs} \boldsymbol{E}_{rs} \right] \\
&= \sum_{r=1}^{M} \sum_{s=1}^{M} h_{rs} (\delta_{rh} \boldsymbol{E}_{ps} - \delta_{ps} \boldsymbol{E}_{rh}) \\
&= \sum_{s=1}^{M} h_{hs} \boldsymbol{E}_{ps} - \sum_{r=1}^{M} h_{rp} \boldsymbol{E}_{rh}
\end{aligned} \tag{95}$$

So

$$\langle 0 | [\boldsymbol{E}_{ph}, \boldsymbol{H}_0] | 0 \rangle = h_{hp} (w_p - w_h) \tag{96}$$

Similarly using:

$$\begin{aligned}
[\boldsymbol{E}_{ph}, \boldsymbol{E}_{rstu}] &= [\boldsymbol{E}_{ph}, \boldsymbol{E}_{rs} \boldsymbol{E}_{tu} - \delta_{ts} \boldsymbol{E}_{ru}] \\
&= \delta_{hr} \boldsymbol{E}_{ps} \boldsymbol{E}_{tu} - \delta_{ps} \boldsymbol{E}_{rh} \boldsymbol{E}_{tu} + \delta_{ht} \boldsymbol{E}_{rs} \boldsymbol{E}_{pu} - \delta_{pu} \boldsymbol{E}_{rs} \boldsymbol{E}_{th} \\
&\quad - \delta_{ts} \delta_{hr} \boldsymbol{E}_{pu} + \delta_{ts} \delta_{pu} \boldsymbol{E}_{rh} \\
&= \delta_{hr} \boldsymbol{E}_{pstu} - \delta_{ps} \boldsymbol{E}_{rhtu} + \delta_{ht} \boldsymbol{E}_{rspu} - \delta_{pu} \boldsymbol{E}_{rsth}
\end{aligned} \tag{97}$$

we have

$$\begin{aligned}
[\boldsymbol{E}_{ph}, \boldsymbol{V}] &= \left[\boldsymbol{E}_{ph}, \tfrac{1}{2} \sum_{r=1}^{M} \sum_{s=1}^{M} \sum_{t=1}^{M} \sum_{u=1}^{M} V_{rstu} \boldsymbol{E}_{rstu} \right] \\
&= \tfrac{1}{2} \left(\sum_{s=1}^{M} \sum_{t=1}^{M} \sum_{u=1}^{M} V_{hstu} \boldsymbol{E}_{pstu} - \sum_{r=1}^{M} \sum_{t=1}^{M} \sum_{u=1}^{M} V_{rptu} \boldsymbol{E}_{rhtu} \right. \\
&\quad \left. + \sum_{r=1}^{M} \sum_{s=1}^{M} \sum_{u=1}^{M} V_{rshu} \boldsymbol{E}_{rspu} - \sum_{r=1}^{M} \sum_{s=1}^{M} \sum_{t=1}^{M} V_{rstp} \boldsymbol{E}_{rsth} \right)
\end{aligned} \tag{98}$$

after relabeling sums and noting $V_{rstu} = V_{turs}$ and $\boldsymbol{E}_{rstu} = \boldsymbol{E}_{turs}$ we have:

$$\begin{aligned}
[\boldsymbol{E}_{ph}, \boldsymbol{V}] &= \sum_{s=1}^{M} \sum_{t=1}^{M} \sum_{u=1}^{M} V_{hstu} \boldsymbol{E}_{pstu} - \sum_{r=1}^{M} \sum_{t=1}^{M} \sum_{u=1}^{M} V_{rptu} \boldsymbol{E}_{rhtu} \\
&= \sum_{r=1}^{M} \sum_{s=1}^{M} \sum_{t=1}^{M} \sum_{u=1}^{M} (V_{hstu} \delta_{r,p} - V_{rptu} \delta_{s,h}) \boldsymbol{E}_{rstu}
\end{aligned} \tag{99}$$

Defining $[\boldsymbol{E}_{ph}, \boldsymbol{V}] = \boldsymbol{K}_2$, and $K_{rstu} = (V_{hstu}\delta_{r,p} - V_{rptu}\delta_{s,h})$ we can substitute into Eq. (135) from Appendix A to evaluate $\langle 0|\boldsymbol{K}_2|0\rangle$. Noting:

$$K_{rrtt} = (V_{hrtt}\delta_{r,p} - V_{rptt}\delta_{r,h}) \quad \text{and} \quad K_{rttr} = (V_{httr}\delta_{r,p} - V_{rptr}\delta_{t,h})$$

$$\begin{aligned}\langle 0|[\boldsymbol{E}_{ph}, \boldsymbol{V}]|0\rangle &= \tfrac{1}{2}\sum_{t=1}^{M} V_{hptt}w_p w_t - \tfrac{1}{2}\sum_{t=1}^{M} V_{hptt}w_h w_t V_{rptu} \\ &\quad - \tfrac{1}{2}\sum_{t=1}^{M} V_{http}\min(w_p, w_t) + \tfrac{1}{2}\sum_{r=1}^{M} V_{rphr}\min(w_r, w_h) \qquad (100)\end{aligned}$$

Employing $V_{rstu} = V_{turs}$ and minor algebra we have:

$$\langle 0|[\boldsymbol{E}_{ph}, \boldsymbol{V}]|0\rangle = (w_p - w_h)\sum_{t=1}^{M} V_{hptt}w_t - \sum_{t=1}^{M} V_{http}(\min(w_p, w_t) - \min(w_t, w_h)) \qquad (101)$$

Therefore,

$$\begin{aligned}\langle 0|[\boldsymbol{E}_{ph}, \boldsymbol{H}]|0\rangle &= (w_p - w_h)h_{hp} + (w_p - w_h)\sum_{t=1}^{M} V_{hptt}w_t \\ &\quad - \sum_{t=1}^{M} V_{http}(\min(w_p, w_t) - \min(w_t, w_h)) \qquad (102)\end{aligned}$$

Often we have real parameters h_{rs} and V_{rstu}. We note that since:

$$\langle 0|[\boldsymbol{E}_{ph}, \boldsymbol{H}]|0\rangle^* = -\langle 0|[\boldsymbol{E}_{hp}, \boldsymbol{H}]|0\rangle \qquad (103)$$

we have in the case of *real* parameters that:

$$\begin{aligned}(1/2)\langle 0|[E_{ph} - E_{hp}, H]|0\rangle &= (w_p - w_h)h_{hp} + (w_p - w_h)\sum_{t=1}^{M} V_{hptt}w_t \\ &\quad - \sum_{t=1}^{M} V_{http}(\min(w_p, w_t) - \min(w_t, w_h)) \qquad (104)\end{aligned}$$

and

$$(1/2)\langle 0|[\boldsymbol{E}_{ph} + \boldsymbol{E}_{hp}, \boldsymbol{H}]|0\rangle = 0 \qquad (105)$$

We (partially) define a Hermitian Fock operator $\boldsymbol{F} = \Sigma F_{hp}\boldsymbol{E}_{hp}$ by the property:

$$\langle 0|[\boldsymbol{E}_{ph}, \boldsymbol{H}]|0\rangle = \langle 0|[\boldsymbol{E}_{ph}, \boldsymbol{F}]|0\rangle \qquad (106)$$

Since, $\langle 0|[\boldsymbol{E}_{ph}, \boldsymbol{F}]|0\rangle = F_{hp}(w_p - w_h)$ we must have in the case $w_p \neq w_h$ that:

$$F_{hp} = h_{hp} + \sum_{t=1}^{M} V_{hptt}w_t - (w_p - w_h)^{-1}\sum_{t=1}^{M} V_{http}(\min(w_p, w_t) - \min(w_t, w_h)) \qquad (107)$$

For $w_p = w_h$ we have $\langle 0|[E_{ph}, F]|0\rangle = \langle 0|[E_{ph}, H]|0\rangle = 0$ a-priori, and the corresponding value F_{hp} is *not* determined by the relation above.

Again we can formally extend the equations to real values of w_r. Taking the limit w_h tending to w_p gives a definition of F_{hp} when $h \neq p$ and $w_h = w_p$. Specifically in this case:

$$F_{hp} = h_{hp} + \sum_{t=1}^{M} V_{hptt}w_t - \left(\sum_{w > w_p = w_h}\ \sum_{\substack{t \\ w_t = w}} V_{http} + \tfrac{1}{2}\sum_{\substack{t \\ w_t = w_p = w_h}} V_{http}\right) \qquad (108)$$

Taking:

$$F_{rr} = h_{rr} + \sum_{t=1}^{M} V_{rrtt} w_t - \left(\sum_{w > w_r} \sum_{\substack{t \\ w_t = w}} V_{rttr} + \tfrac{1}{2} \sum_{\substack{t \\ w_t = w_r}} V_{rttr} \right. \tag{109}$$

is totally consistent with derivative of the ground state energy in respect to w_r and is invariant under unitary orbital transformations within the same weight. We emphasize that formally *any* choice may be made for F_{ph} when $w_p = w_h$. Alternate choices would be to use forward and backward differences instead of a derivative (i.e., orbital energies representing electron affinities and ionizations, respectively).

5.3.4 Density matrices and implementation of Hartree–Fock equations. The sums a written in Eq. (93) as well as other equations derived so far are inefficient for the purpose of computation. For instance we can employ symmetries $V_{rrtt} = V_{ttrr}$ and $V_{trrt} = V_{rttr}$. Furthermore, since it is likely that only a few distinct values of w are possible in a given problem (i.e., for typical atomic and molecular problems $w = 0, 1, 2$ only) we will explicitly sum over possible values of w_r and w_t, giving a more complicated but efficient form of Eq. (93).

$$\langle 0|\boldsymbol{H}|0\rangle = \sum_{r=1}^{M} w_r h_{rr} + \tfrac{1}{2} \sum_{w} (w^2 - w) \sum_{\substack{r \\ w_r = w}} V_{rrrr} + \sum_{w} \sum_{\substack{r < t \\ w_r = w \\ w_r = w}} (w^2 V_{rrtt} - w V_{rttr})$$

$$+ \sum_{w < w'} \sum_{\substack{r \\ w_r = w}} \sum_{\substack{t \\ w_t = w'}} w(w' V_{rrtt} - V_{rttr}) \tag{110}$$

where $\sum_{w_r = w} {}_r$ is a sum over all orbitals r with weight w.

In practice, the V_{rstu} are usually not *directly* computed on the current estimate of the Hartree–Fock orbitals but on the most convenient orbital basis for computation (for instance atomic orbitals). Let $\{|x_A\rangle\}$ denote an alternate orthonormal basis for the orbitals. Let $\mathscr{h}_{xy}$ and $\mathscr{V}_{xyzw}$ denote the corresponding parameters of the Hamiltonian. Then:

$$h_{rs} = \sum_{x=1}^{M} \sum_{y=1}^{M} \mathscr{h}_{xy} \langle s|x_A\rangle \langle y_A|r\rangle \tag{111a}$$

$$V_{rrtt} = \sum_{x=1}^{M} \sum_{y=1}^{M} \sum_{z=1}^{M} \sum_{q=1}^{M} \mathscr{V}_{xyzq} \langle r|x_A\rangle \langle y_A|r\rangle \langle t|z_A\rangle \langle q_A|t\rangle \tag{111b}$$

$$V_{rttr} = \sum_{x=1}^{M} \sum_{y=1}^{M} \sum_{z=1}^{M} \sum_{q=1}^{M} \mathscr{V}_{xyzw} \langle r|x_A\rangle \langle y_A|t\rangle \langle t|z_A\rangle \langle q_A|r\rangle \tag{111c}$$

Defining first-order density matrix elements as [28]:

$$\varrho(w)_{yx} = \sum_{\substack{r \\ w_r = w}} \langle r|x_A\rangle \langle y_A|r\rangle \quad \text{and} \quad \varrho_{yx} = \sum_{w} w \varrho(w)_{yx} \tag{112}$$

we have:

$$\langle 0|\boldsymbol{H}|0\rangle = \sum_{x=1}^{M} \sum_{t=1}^{M} \varrho_{yx} \mathscr{h}_{xy} + \tfrac{1}{2} \sum_{x=1}^{M} \sum_{y=1}^{M} \sum_{z=1}^{M} \sum_{q=1}^{M} \mathscr{V}_{xyzw}$$

$$\times \left(\varrho_{yx} \varrho_{qz} - \sum_{w} \sum_{w'} \min(w, w') \varrho(w)_{qx} \varrho(w')_{yz} \right) \tag{113}$$

From a theoretical standpoint, the ground state energy depends only on the density matrices $\varrho(w)$ for $w \geqslant 1$ and the values of $\mathscr{V}_{xyzq}$. The density matrices therefore may be considered as the unknown rather than the orbitals and the equations may be solved for the density matrices only. The same comments obviously apply to the derivatives of the ground state energy. Such an approach was originally formulated by Löwdin [2] for the fermion case and developed further by later authors [9].

From a practical standpoint, each density matrix requires order of M^2 storage and M^3 computational cost. For a system with few distinct values of w the computation time of the Hartree–Fock energy is of order M^4. In contrast, the direct transformation of the second degree Hamiltonian itself requires order of M^5 computation time and M^4 storage.

Similarly, the elemements of the Fock matrix on the basis $\{|x_A\rangle\}$ may be calculated from Eq. (107) and the density matrices via:

$$\mathscr{F}_{xy} = \mathscr{h}_{xy} + \sum_{z=1}^{M} \sum_{q=1}^{M} \varrho_{qz} \mathscr{V}_{xyzq} - \mathscr{D}_{xy} \tag{114}$$

where the matrix elements $\mathscr{D}_{xy}$ are calculated in the following steps.

First the quantities:

$$\mathscr{G}_{xy}(w) = \sum_{z=1}^{M} \sum_{q=1}^{M} \varrho_{qz}(w) \mathscr{V}_{xqzy} \tag{115}$$

are calculated defining matrices $[\mathscr{G}(w)]$. The matrices are transformed back to the basis representing the present estimate of the Fock orbitals via:

$$[G(w)] = [S]^{\dagger}[\mathscr{G}(w)][S] \tag{116}$$

where $[S]$ is the unitary overlap matrix between the two orbital basis. Matrix elements:

$$D_{hp} = (w_p - w_h)^{-1} \sum_{w} (\min(w_p, w) - \min(w, w_h)) G_{hp}(w) \tag{117}$$

are calculated and the corresponding matrix transformed back to give:

$$[\mathscr{D}] = [S][D][S]^{\dagger} \tag{118}$$

Similar techniques may be used on the second order variation and Eq. (144).

5.4 Hartree–Fock theory for the closed-shell Gel'fand reference state

5.4.1 The general equations. For a $U(M)$ extreme weight state formed out of N boxes formed into w columns each length N/w Eq. (109) reduces to:

$$\langle 0|\boldsymbol{H}|0\rangle = w \sum_{r=1}^{N/w} h_{rr} + \tfrac{1}{2} \sum_{r=1}^{N/w} \sum_{t=1}^{N/w} (w^2 V_{rrtt} - w V_{rttr}) \tag{119}$$

For a two column freeon singlet state $w = 2$.

$$\langle 0|\boldsymbol{H}|0\rangle = 2 \sum_{r=1}^{N/2} h_{rr} + \sum_{r=1}^{N/2} \sum_{t=1}^{N/2} (2V_{rrtt} - V_{rttr}) \tag{120}$$

Similarly:

$$F_{hp} = h_{hp} + w \sum_{t=1}^{N/2} V_{hptt} - \sum_{t=1}^{N/2} V_{http} \tag{121}$$

5.4.2 Ethylene. For ethylene the HF orbitals are completely determined by symmetry; i.e.:

$$|HF\rangle = \boxed{1}\boxed{1}$$

For an even linear polyene with half filling ($M = N$) in a singlet state, the Hartree–Fock energy employing molecular orbitals is given by:

$$E_{\text{Hartree-Fock}} = \frac{M}{4}x + 2(|x| - 1)\left(\frac{1}{\sin\left(\dfrac{\pi}{2(M+1)}\right)} - 1\right) \tag{122}$$

In this case, the orbitals are minima for $0 \leqslant x < 1$. But we emphasize that in general the orbitals are rigourously extremum, but need not be minima.

For ethylene ($M = N = 2$):

$$E_{\text{Hartree-Fock}} = \frac{x}{2} + 2(|x| - 1)$$

The exact, Hartree–Fock and correlation energies for ethylene are plotted in Fig. 4.

For linear butadiene ($M = N = 4$):

$$E_{\text{Hartree-Fock}} = x + 4.472(|x| - 1)$$

The exact, Hartree–Fock and correlation energies for butadiene are plotted in Fig. 5.

In the limit of large M, $E_{\text{Hartree-Fock}}$ is approximately:

$$E_{\text{Hartree-Fock}} = \frac{M}{4}x + \frac{4M(|x| - 1)}{\pi} \tag{123}$$

5.5 Hartree–Fock theory for the open shell ($S > 0$) Gel'fand reference state

5.5.1 The general equations. For a two column freeon singlet state $w = 2, 1, 0$. Denote double occupied orbitals by d and d', singles by s and s' and unoccupied

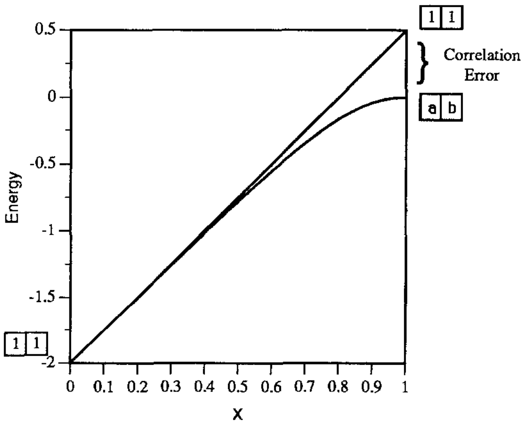


Fig. 4. Correlation energy for neutral ethylene

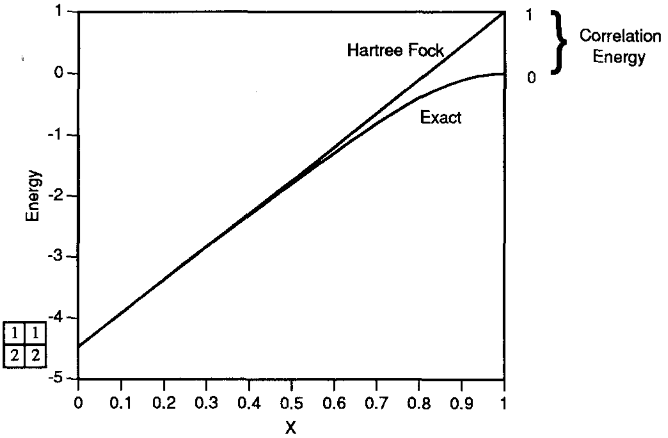


Fig. 5. Correlation energy for linear butadiene

orbitals by u and u'. Equation (109) reduces to:

$$\langle 0|\boldsymbol{H}|0\rangle = 2\sum_{d} h_{dd} + \sum_{s} h_{ss} + \tfrac{1}{2}\sum_{dd'} (4V_{ddd'd'} - 2V_{dd'd'd}) + \tfrac{1}{2}\sum_{ss'} (V_{sss's'} - V_{ss's's}) + \sum_{ds} (2V_{ssdd} - V_{sdds}) \tag{124}$$

5.5.2 The allyl radical. For an odd linear polyene with half filling ($N = M$) in a doublet state, the Hartree–Fock energy employing molecular orbitals is given by:

$$E_{\text{Hartree–Fock}} = \left(\frac{M}{4} - \frac{1}{2(M+1)}\right)x + 2(|x|-1)\left(\cot\text{an}\left(\frac{\pi}{2(M+1)}\right) - 1\right) \tag{125}$$

We emphasize that the orbitals are rigourously extrenum, but need not be minima.

In the limit of large M, $E_{\text{Hartree–Fock}}$ is approximately:

$$E_{\text{Hartree–Fock}} \approx \frac{M}{4}x + \frac{4M(|x|-1)}{\pi}$$

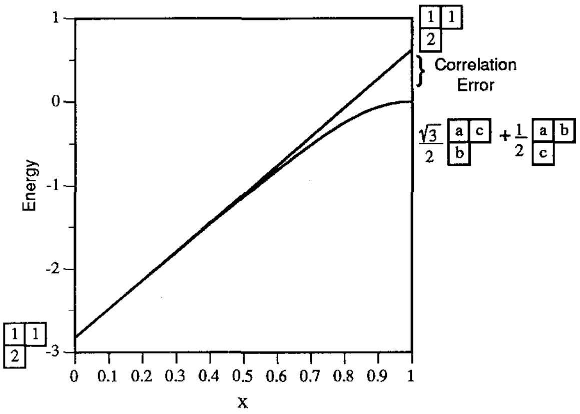


Fig. 6. Correlation energy for the allyl radical

For allyl doublet state ($N = M = 3$) we have:

$$E_{\text{Hartree-Fock}} = 5x/8 + 2\sqrt{2}(|x| - 1)$$

The exact, Hartree–Fock and correlation energies for allyl are shown in Fig. 6.

6. Conclusion

We have presented the freeon unitary group formulation of nonrelativistic quantum chemistry and have applied it to Hartree–Fock theory.

Appendix A: One and two bodied matrix elements on extreme weight states

While there are many methods of calculating matrix elements on unitary group bases, we will employ the simplest self-contained method applicable to this special case.

A.1 Matrix elements of operators of degree one in the generators

Let $|0\rangle$ be an extreme weight state of $U(M)$ with weight $\{w_1, w_2, w_3, \ldots, w_M\}$.
We will be calculating:

$$\langle 0|\boldsymbol{K}_1|0\rangle$$

where

$$\boldsymbol{K}_1 = \sum_{r=1}^{M} \sum_{s=1}^{M} K_{rs}\boldsymbol{E}_{rs} \tag{126}$$

and $|0\rangle$ is an extreme weight.

But, by the definition of extreme weight state (82) and $\langle 0|\boldsymbol{E}_{rs}|0\rangle^* = \langle 0|\boldsymbol{E}_{sr}|0\rangle$ we have:

$$\langle 0|\boldsymbol{E}_{rs}|0\rangle = \delta_{r,s} w_r \tag{127}$$

Hence,

$$\langle 0|\boldsymbol{E}_{rs}|0\rangle = \sum_{r=1}^{M} \boldsymbol{K}_{rr} w_r \tag{128}$$

A.2 Matrix elements of symmetric operators of degree two in the generators

We define the operator:

$$\boldsymbol{E}_{rstu} \equiv \boldsymbol{E}_{rs}\boldsymbol{E}_{tu} - \delta_{ts}\boldsymbol{E}_{ru} = \boldsymbol{E}_{tu}\boldsymbol{E}_{rs} - \delta_{ru}\boldsymbol{E}_{ts} = \boldsymbol{E}_{turs} \tag{129}$$

The equality used in the definition above follows from $[\boldsymbol{E}_{rs}, \boldsymbol{E}_{tu}] = \delta_{ts}\boldsymbol{E}_{ru} - \delta_{ru}\boldsymbol{E}_{ts}$.

We will be calculating:

$$\langle 0|\boldsymbol{K}_2|0\rangle$$

where

$$K_2 = \tfrac{1}{2} \sum_{r=1}^{M} \sum_{s=1}^{M} \sum_{t=1}^{M} \sum_{u=1}^{M} K_{rstu} E_{rstu} \tag{130}$$

and $|0\rangle$ is an extreme weight.

We will require the matrix elements $\langle 0|E_{rstu}|0\rangle$. To evaluate this matrix element we break it into three cases.

If $t \neq u$ and $w_t \geqslant w_u$ then:

$$\begin{aligned}\langle 0|E_{rstu}|0\rangle &= \langle 0|(E_{rs}E_{tu} - \delta_{ts}E_{ru})|0\rangle \\ &= 0 - \delta_{ts}\langle 0|E_{ru}|0\rangle = -\delta_{ts}\delta_{ru}w_u\end{aligned} \tag{131a}$$

If $t \neq u$ and $w_t \leqslant w_u$ then:

$$\begin{aligned}\langle 0|E_{rstu}|0\rangle &= \langle 0|(E_{tu}E_{rs} - \delta_{ru}E_{ts})|0\rangle \\ &= 0 - \delta_{ru}\langle 0|E_{ts}|0\rangle = -\delta_{ru}\delta_{ts}w_t\end{aligned} \tag{131b}$$

If $t = u$ then:

$$\begin{aligned}\langle 0|E_{rstt}|0\rangle &= \langle 0|E_{rs}E_{tt} - \delta_{ts}E_{rt}|0\rangle \\ &= \delta_{rs}w_r w_t - \delta_{ts}\delta_{rt}w_r = \delta_{rs}(w_r w_t - \delta_{rt}w_r)\end{aligned} \tag{131c}$$

The cases $w_t \geqslant w_u$ and $w_t \leqslant w_u$ are combined into one expression giving:

$$\text{if } t \neq u \text{ then } \langle 0|E_{rstu}|0\rangle = -\delta_{ru}\delta_{ts}\min(w_u, w_t) \tag{132}$$

which can be written as one expression:

$$\begin{aligned}\text{and}\quad \langle 0|E_{rstu}|0\rangle &= \delta_{rs}\delta_{tu}(w_r w_t - \delta_{rt}w_r) + (\delta_{tu} - 1)\delta_{ru}\delta_{ts}\min(w_u, w_t) \\ &= \delta_{rs}\delta_{tu}w_r w_t - \delta_{ru}\delta_{ts}\min(w_u, w_t)\end{aligned} \tag{133}$$

Note: $\langle 0|E_{rstu}|0\rangle = 0$ unless r, s, t, u are *all* orbitals.

$$\begin{aligned}\langle 0|K_2|0\rangle &= \tfrac{1}{2} \sum_{r=1}^{M} \sum_{s=1}^{M} \sum_{t=1}^{M} \sum_{u=1}^{M} K_{rstu}\langle 0|E_{rstu}|0\rangle \\ &= \tfrac{1}{2} \sum_{r=1}^{M} \sum_{s=1}^{M} \sum_{t=1}^{M} \sum_{u=1}^{M} K_{rstu}(\delta_{rs}\delta_{tu}w_r w_t - \delta_{ru}\delta_{ts}\min(w_u, w_t))\end{aligned} \tag{134}$$

Which simplifies into:

$$\langle 0|K_2|0\rangle = \tfrac{1}{2} \sum_{r=1}^{M} \sum_{t=1}^{M} K_{rrtt}w_r w_t - \tfrac{1}{2} \sum_{r=1}^{M} \sum_{t=1}^{M} K_{rttr}\min(w_r, w_t) \tag{135}$$

Appendix B: Stability matrix elements

We evaluate $[E_{p'h'}, [E_{ph}, H_0]]$ as follows. $[E_{ph}, H_0]$ was evaluated in Eq. (95); therefore we have:

$$\begin{aligned}[E_{p'h'}, [E_{ph}, H_0]] &= \sum_{s=1}^{M} h_{hs}[E_{p'h'}, E_{ps}] - \sum_{r=1}^{M} h_{rp}[E_{p'h}, E_{rh}] \\ &= \delta_{ph'} \sum_{s=1}^{M} h_{hs}E_{p's} - h_{hp'}E_{ph'}E_{ph'} - h_{h'p}E_{p'h} + \delta_{p'h} \sum_{r=1}^{M} h_{rp}E_{rh'}\end{aligned} \tag{95}$$

From Eq. (96) we have:

$$\langle 0|[\boldsymbol{E}_{p'h'}, [\boldsymbol{E}_{ph}, \boldsymbol{H}_0]]|0\rangle = \delta_{ph'}h_{hp'}(w_{p'} - w_p) + \delta_{p'h}h_{h'p}(w_{h'} - w_h) \qquad (136)$$

Similarly, by Eq. (99):

$$[\boldsymbol{E}_{ph}, \boldsymbol{V}] = \sum_{r=1}^{M}\sum_{s=1}^{M}\sum_{t=1}^{M}\sum_{u=1}^{M}(V_{hstu}\delta_{r,p} - V_{rptu}\delta_{s,h})\boldsymbol{E}_{rstu}$$

Defining $V_{rstu}(ph) = [(V_{hstu}\delta_{r,p} - V_{rptu}\delta_{s,h}) + (V_{hurs}\delta_{t,p} - V_{tprs}\delta_{u,h})]$ and noting $V_{rstu}(ph) = V_{turs}(ph)$ we have by Eq. (99) again that:

$$[\boldsymbol{E}_{p'h'}, [\boldsymbol{E}_{ph}, \boldsymbol{V}]] = \sum_{r=1}^{M}\sum_{s=1}^{M}\sum_{t=1}^{M}\sum_{u=1}^{M}(V_{h'stu}(ph)\delta_{r,p'} - V_{rp'tu}(ph)\delta_{s,h'})\boldsymbol{E}_{rstu} \qquad (137)$$

Defining $\boldsymbol{K}_2 = [E_{p'h'}, [E_{ph}, V]]$ and:

$$K_{rstu} = 2(V_{h'stu}(ph)\delta_{r,p'} - V_{rp'tu}(ph)\delta_{s,h'}) \qquad (138)$$

Noting:

$$K_{rrtt} = 2(V_{h'rtt}(ph)\delta_{r,p'} - V_{rp'tt}(ph)\delta_{r,h'})$$

and

$$K_{rttr} = 2(V_{h'ttr}(ph)\delta_{r,p'} - V_{rp'tr}(ph)\delta_{t,h'})$$

we may employ Eq. (135) to give

$$\langle 0|\boldsymbol{K}_2|0\rangle = \sum_{t=1}^{M}(V_{h'p'tt}(ph)w_{p'} - V_{h'p'tt}(ph)w_{h'})w_t$$
$$- \sum_{t=1}^{M} V_{h'ttp'}(ph)\min(w_{p'}, w_t) + \sum_{r=1}^{M} V_{rp'h'r}(ph)\min(w_r, w_{h'}) \qquad (139)$$

using $V_{rstu}(ph) = V_{turs}(ph)$ we have:

$$\langle 0|\boldsymbol{K}_2|0\rangle = \sum_{t=1}^{M}[(w_{p'} - w_{h'})V_{h'p'tt}(ph) - (\min(w_{p'}\ w_t) - \min(w_{h'}, w_t))V_{h'ttp'}(ph)] \qquad (140)$$

substituting:

$$V_{h'p'tt}(ph) = [(V_{hp'tt}\delta_{h',p} - V_{h'ptt}\delta_{p',h}) + (V_{hth'p'}\delta_{t,p} - V_{tph'p'}\delta_{t,h})] \qquad (141)$$

and

$$V_{h'ttp'}(ph) = [(V_{http'}\delta_{h',p} - V_{h'ptp'}\delta_{t,h}) + (V_{hp'h't}\delta_{t,p} - V_{tph't}\delta_{p'h})] \qquad (142)$$

$$\langle 0|\boldsymbol{K}_2|0\rangle = \Bigg[\delta_{h',p}\left(\sum_{t=1}^{M}(w_{p'} - w_{h'})w_t V_{hp'tt} - (\min(w_{p'}, w_t) - \min(w_{h'}, w_t))V_{http'}\right)$$
$$- \delta_{p',h}\left(\sum_{t=1}^{\mu}(w_{p'} - w_{h'})w_t V_{h'ptt} - (\min(w_{p'}, w_t) - \min(w_{h'}, w_t))V_{h'ttp}\right)$$
$$+ (w_{p'} - w_{h'})w_p V_{hph'p'} - (\min(w_{p'}, w_p) - \min(w_{h'}, w_p))V_{hp'h'p}$$
$$- ((w_{p'} - w_{h'})w_h V_{hph'p'} - (\min(w_{p'}, w_h) - \min(w_{h'}, w_h))V_{hp'h'p})\Bigg] \qquad (143)$$

Therefore:

$$\begin{aligned}\langle 0|E_{p'h'}, [E_{ph}, V]]|0\rangle = \Bigg[& \delta_{h',p} \sum_{t=1}^{M} ((w_{p'} - w_{h'})w_t V_{hp'tt} - (\min(w_{p'}, w_t) \\ & - \min(w_{h'}, w_t))V_{http'}) - \delta_{p',h} \sum_{t=1}^{M} ((w_{p'} - w_{h'})w_t V_{h'ptt} \\ & - (\min(w_{p'}, w_t) - \min(w_{h'}, w_t))V_{h'ttp}) \\ & + (w_{p'} - w_{h'})(w_p - w_h)V_{hph'p'} - (\min(w_{p'}, w_p) \\ & - \min(w_{p'}, w_h) - \min(w_{h'}, w_p) + \min(w_{h'}, w_h))V_{hp'h'p} \Bigg] \end{aligned} \tag{144}$$

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