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Hamiltonian as a Hessian on the Hilbert space, eigenvectors as critical points, and their relation to topological invariants in the variation method

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If a quantum vector varies in the Hilbert space, as trial functions do in the variational method, a vector field gets defined whose critical points are the eigenvectors of the Hamiltonian. The numbers of each type of critical point (minima, maxima, saddle points of various "indices") are related to the topology of the compact variety, the closed multidimensional surface on which the trial vectors wander when they are restricted to unit normalization. The "global" results from that approach are compared with those of the "local" theory in which the type of each critical point is obtained from the Hessian on the Hilbert space whose eigenvalues are derived in terms of those of the Hamiltonian involved in the vector field. In a configuration-interaction (CI) problem for example, the type of saddle point each "excited state" represents is determined.

Key words: Topological invariants—global variation method—Hessian—critical point

1. Introduction

The variational method allows the ground state of a Hamiltonian H to be calculated by the minimization of the functional

$$E[\tilde{u}] \leq \langle \tilde{u}|H|\tilde{u}\rangle / \langle \tilde{u}|\tilde{u}\rangle. \tag{1}$$

For excited states however, the varied state needs to be kept orthogonal to all the lower eigenvectors. This is automatic if there are no lower states of the same symmetry. Otherwise there is a serious difficulty. As the lower states are not exactly known, during variations one may slip towards some lower state. Practical

methods for dealing with these problems were given in the "Variation-Perturbation Method for Excited States" by this writer [1], and in the difficult cases of some of the excited states of atoms treated by the "Non-Closed Shell Many-Electron Theory" [2], by Luken and Sinanoğlu [3] and by Luken [4]. Earlier methods dealing with the variational approach, e.g. those of Eckart [5] and the theorem of MacDonald [6] had been elegantly reviewed by Löwdin [7]. We shall not need to go into any of the methods mentioned above in any detail. Suffice it to say that it is crucial to know readily and before any extensive computation, the nature and type of extremum a given higher eigenvalue represents. Most of the eigenvalues turn out to be saddle points, only the highest one a maximum (in the case of a finite dimensional subspace of the Hilbert space) as seen below.

For each eigenvalue we determine the directions in the Hilbert space in which the energy goes up and those in which it goes down, and thereby also the "index" of each saddle point. In the last section, the topology of the $(n-1)$-dim. variety or closed surface in the n-dim. subspace C_n of the Hilbert space $\mathscr{L}_2$, over which the variations occur is related to finding the numbers of each kind of critical point (minima, maxima, saddle points of various indices, ...).

2. Unnormalized variations of vectors over C_n and the Hamiltonian as a Hessian

Let $\{|e_i\rangle\}$ be an orthogonal (O.N.) basis for $C_n \subset \mathscr{L}_2$. Then with any

$$|u\rangle = \sum_i^n c_i |e_i\rangle \tag{2}$$

$$\varepsilon \equiv \langle u|H|u\rangle = \sum_{i,j}^n c_i^* c_j H_{ij}. \tag{3}$$

The critical points of the scalar field $\varepsilon[u]$ on C_n occur at

$$\frac{\partial \varepsilon}{\partial c_i} = 2H_{ij}c_j = 0 \quad \text{for all } i \tag{4}$$

(taking $\boldsymbol{c}$ to be real).

Thus $\{H|u\rangle\}$ may be viewed as a vector field defined on C_n.

$H|u\rangle = 0$ has only the trivial solution $|u\rangle = 0$, i.e. $\{c_i = 0 \text{ for } 1 \leq i \leq n\}$ unless $\det H = 0$. In the latter case there are a number of zero eigenvalues and $H|u_k(0)\rangle = 0$.

The Hessian $\mathscr{H}$ becomes just the Hamiltonian itself:

$$\mathscr{H}_{ij} \equiv \frac{\partial^2 \varepsilon}{\partial c_i \, \partial c_j} = 2H_{ij}. \tag{5}$$

The numbers of negative, zero and positive eigenvectors $\{\eta_-, \eta_0, \eta_+\}$ of the Hessian determine the nature of the critical point, the solution(s) of Eq. (4). But

these are precisely the eigenvalue types of the Hamiltonian $\{n_-, n_0, n_+\}$. Thus we have

Theorem 1. *For the arbitrary (unnormalized) variations of a vector* $|u\rangle$ *in* $C_n \subset \mathscr{L}_2$ *the Hamiltonian* H *is* $(\frac{1}{2}x)$ *the Hessian of the functional* $\langle u|H|u\rangle \equiv \varepsilon[u]$ *(where* $\langle u|u\rangle$ *in general* $\neq 1$*). The critical point(s) of* $\varepsilon[u]$ *occur at the* $\lambda_k = 0$ *eigenvectors of* H*, i.e.* $H|u_k\rangle = 0$.

Proof. Eqs. (2)–(5).

Corollary 1-1. *If* $|H| \neq 0$ *so that rank* $H = n$*, the only critical point in* C_n *is at the origin,* $\{c_i = 0\}$*. This is then a saddle point of index* $\eta_- = n_-$*. In the* n_- *directions in* C_n*, along the eigenvectors of* H *with negative eigenvalues,* $\varepsilon[u]$ *comes down.*

Along the other directions pointed by the positive eigenvalue vectors ($n_+ = n - n_-$ *of them),* $\varepsilon[u]$ *goes up.*

Proof. $\eta_0 = n_0 = 0$; and + and − eigenvectors of $\mathscr{H}$ and H are the same. Index of the saddle point $= \eta_- = n_-$. (For $|H| \neq 0$ the only solution of $H|u_k\rangle = 0$ is $|u_k\rangle = 0$, i.e. the origin $\{c_i = 0\}$.

Corollary 1-2. *If* $|H| = 0$*, rank* $H < n$*. There are one or more, say* n_0 *non-trivial* $\lambda_k = 0$ *eigenvectors. But then the Hessian too will have* $\eta_0 = n_0$ *zero eigenvalues. Such critical points are said to be "degenerate". As there are a continuous family of them for a family of* $|u_k\rangle$ *differing in normalization constants (in the complex case, also in phases these making up a "ray"), the critical points are also "non-isolated". In the other* n_- *and* n_+ *eigenvector directions* $\varepsilon[u]$ *still goes down and up respectively.*

Remark. Since the vectors $|u\rangle$ are not normalized in $\varepsilon[u]$, only the directions along eigenvectors $|u_i\rangle$ are defined in C_n. A direction $\{\gamma|u_i\rangle;\ 0 < \gamma < \infty\}$ passes through the eigenvector *point* $|u_i\rangle$ which is for the γ value such that $\langle u_i|u_i\rangle = 1$.

Remark. $\varepsilon[u] = c_i c_j H^{ij}$ for c real (tensorial summation convention) is an $(n-1)$ dim. conic surface for each specified value of $\varepsilon > 0$. The type of conic is determined by the eigenvalue type numbers $\{n_-, n_0, n_+\}$; e.g. if $n_- = 0$, $n_0 = 0$, $n_+ = n$ we have an $(n-1)$-dim ellipsoid. A concentric family of these surfaces are generated as ε takes on different values. For $0 \leq \varepsilon < \varepsilon_{\max}$ we have the inside of the solid ellipsoidal shape. Other conics result for n_-, $n_0 \neq 0$. The "eigenvector rays" $\{\gamma|u_i\rangle\}$ correspond to principal axes of the $(n-1)$ conic solid object.

3. Variations of vectors constrained to unit normalizations

Let now all $|u\rangle$ in the variation method and in $\varepsilon[u] = \langle u|H|u\rangle$ to be constrained so as

$$d[u] \equiv \langle u|u\rangle = \sum_{i \geq 1}^{n} c_i^2 = 1. \tag{6}$$

Then also we have $E[u] = \varepsilon[u]$ where $E[u] \equiv \langle u|H|u\rangle / \langle u|u\rangle$ for arbitrary $|u\rangle \in C_n$ and $E[u]$ no longer a minimum in general.

Eq. (6) shows that $|u\rangle$, i.e. the coefficients $c=\{c_i\}$ on the O.N. basis $\{|e_i\rangle\}$ are varied subject to Eq. (6), the tips of the u-vectors in C_n stay on the unit-sphere, a surface of dim. (n−1). Unlike the unnormalized or "ray"-variations of the previous section, the vectors now go over a compact closed surface, a compact variety.

The critical points of the field $\varepsilon[u]$ and the Hessian that gives their nature are now different than in the previous section, still related to the Hamiltonian but not the same.

Varying $\varepsilon[u]$ with respect to $|u\rangle$, i.e. the $\{c_i\}$ subject to Eq. (6), we get in the usual way

$$\sum_i^n \left(\frac{\partial \varepsilon}{\partial c_i} - \lambda \frac{\partial d}{\partial c_i}\right) \delta c_i = 0 \tag{7}$$

or

$$\frac{\partial \varepsilon}{\partial c_i} - \lambda \frac{\partial d}{\partial c_i} = 0 \quad \text{for all } i \in \{1, 2, \ldots n\}.$$

From Eqs. (3) and (6), this becomes

$$\sum_{j\geq 1}^n (H_{ij} - \lambda \delta_{ij}) c_j = 0 \quad \text{for all } i.$$

The critical points of $\varepsilon[u] = E[u]$ on the $(n-1)$ unit-sphere now occur where the vector field $\boldsymbol{v}(c_1, c_2, \ldots c_n; \lambda)$, or

$$\boldsymbol{v}(\boldsymbol{c}; \lambda) \equiv (\boldsymbol{H} - \lambda \boldsymbol{I})\boldsymbol{c} \tag{8}$$

is zero on the unit sphere. This happens of course at the eigenvectors (normalized to unity) $|u^{(k)}\rangle$ of H and $\lambda = \lambda^{(k)}$ eigenvalue. It appears therefore there are n critical points on the $(n-1)$-sphere (see however the last section).

The type of each critical point is given by the Hessian $\mathscr{H}_\lambda$ of the scalar field $\varepsilon[u] = E[u]$ s.t. $d[u] = 1$ as in Eq. (9) from Eq. (8).

$$\frac{\partial \boldsymbol{v}}{\partial \boldsymbol{c}} = \boldsymbol{H} - \lambda \boldsymbol{I} = \mathscr{H}_\lambda. \tag{9}$$

[This could have been obtained also as

$$\left[\frac{\partial^2 \varepsilon}{\partial c_i\, \partial c_j} - \mu \frac{\partial^2 d}{\partial c_i\, \partial c_j} = 2(H_{ij} - \mu \delta_{ij})\right].$$

The nature of the critical point $|u^{(k)}\rangle$ at $\lambda = \lambda^{(k)}$ is given by the numbers of $\{+, 0, -\}\{\rho_l^{(k)}\}$ eigenvalues $\{\eta_+, \eta_0, \eta_-\}_\lambda(k)$ of the Hessian evaluated at a given eigenvector of H, i.e. for a given $\lambda = \lambda^{(k)}$, i.e. $\mathscr{H}_{\lambda^{(k)}}$,

$$(\mathscr{H}_{\lambda^{(k)}} - \rho_l^{(k)} I)|w_l^{(k)}\rangle = 0. \tag{10}$$

From Eq. (9), this is

$$\mathcal{H}_{\lambda^{(k)}} - \rho_l^{(k)} I = H - (\lambda^{(k)} + \rho_l^{(k)}) I \tag{11}$$

so that we have $\lambda^{(l)} = \lambda^{(k)} + \rho_l^{(k)}$.

Thus

$$\rho_l^{(k)} = \lambda^{(l)} - \lambda^{(k)}. \tag{12}$$

Theorem 2. *The critical points of the energy functional $E[u]$ on the $(n-1)$-unit sphere (so as to maintain $\langle u|u\rangle = 1$) occur at the eigenvectors $\{|u^{(k)}\rangle\}$ of the Hamiltonian H. The Hessian at the $(k)^{th}$ critical point has n eigenvalues $\rho_l^{(k)}$; $l \in \{1, 2, \ldots n\}$ given by Eq. (12), i.e. the eigenvalues of H less the $(k)^{th}$ fixed one of the critical point.*

Proof. Given just above.

Corollary 2-1. *Suppose all the invariant manifolds under H are one-dimensional (i.e. there are no degenerate eigenvalues of H). Then the first eigenvalue is a minimum (of $E[u]$), the second is a saddle point of index 1, i.e. ($\eta^- = 1$ and $\eta^+ = n-2$), third is a saddle point of $\eta^- = 2$, and so on with the last eigenvalue $\lambda^{(n)}$ a maximum. For the k^{th} eigenvalue of H,*

$$\eta^+(\lambda^{(k)}) = n - k \tag{13a}$$

and

$$\eta^-(\lambda^{(k)}) = k - 1. \tag{13b}$$

Proof. $\rho_l^{(k)} = (\lambda_l - \lambda^{(k)}) > 0$ for $l > k$.

Note that for $l = k$, one has $\rho_l^{(k)} = 0$ so it would appear that $\eta_0(\lambda^{(k)}) = 1$ for each fixed (k). However this simply states that variations in the radial direction on the unit sphere are not permitted, one being constrained to the surface of the sphere. Other directions which are along other $|u^{(k)}\rangle$'s are tangent to the sphere. Their numbers add up to Eqs. (13).

Corollary 2-2. *From Theorems 1 and 2 it is seen that the vector directions $\{\gamma|u^{(k)}\rangle\}$ from the saddle point at the origin $c = 0$ in the unconstrained "ray-variations" of $[u]$ pierce the unit-sphere at the critical points $\{|u^{(k)}\rangle : \langle u^{(k)}|u^{(k)}\rangle = 1\}$ of $E[u]$ on the sphere.*

Proof. The gradient lines $\partial\varepsilon/\partial c$ for the rays $\sum_i^n c_i^2 \neq 1$ start at the origin $c = 0$ as $(\frac{\partial\varepsilon}{\partial c})_0 = 0$, then go up or down according to the eigenvector directions of $(\partial^2\varepsilon/\partial c\, \partial c') = 2H_{ij}$. The critical points of $\varepsilon[u]$ with $d = 1$ are the tips of the $|u^{(k)}\rangle$ vectors on the unit-sphere.

Corollary 2-3. *Suppose $\lambda^{(k)}$ is degenerate, so that $\lambda^{(k-1)} = \lambda^{(k)} = \lambda^{(k+1)} \ldots$. Then the $\lambda^{(k)}$ is a degenerate (in the vector fields sense)* critical point, *also* non-isolated *(as are $(k-1)$ and $(k+1)$]. The $\mathcal{H}_{\lambda^{(k)}}$ has "non-radial" $\rho_l = 0$ eigenvectors. Variations of $|u\rangle$ along $|u^{(k-1)}\rangle$, $|u^{(k)}\rangle$ and $|u^{(k+1)}\rangle$ keep $\varepsilon[u]$ constant. These directions*

constitute a plane, a linear manifold, on the $\varepsilon[u]$ surface at constant $\lambda^{(k)}$. The $\varepsilon[u]$ still goes up or down along the other dimensions $l \neq \{k-1, k, k+1\}$.

Proof. From Eq. (12).

4. Topological invariants of the $(n-1)$ unit sphere in the Hilbert space and their relation to the numbers and indices of the critical points on the energy surface

There are relations between the numbers of critical points of each type on $E[u]$ if $[u]$ variations are confined to the surface of a compact variety (and if $E[u]$ is twice differentiable), and the topological invariants of the variety. Such a global variational theory was developed by the mathematician Marston Morse [8]. Initial notions along such lines had been introduced by Poincaré. The theory is outlined by Milnor [9].

We now explore here how much information can be obtained from the Morse inequalities for the quantum mechanical $E[u]$ minmax problem. To our knowledge this is the first introduction in quantum chemistry of "Morse Theory".

Restricting the $[c]$ to the real scalar field so that $C_n \to V_n$ real vector space of dim $= n$, on the $(n-1)$ unit sphere, the Morse conditions are satisfied. The $[u]$ is on a compact variety, the unit sphere, and $E[c]$ is twice differentiable in c.

The theory becomes far too complicated if some of the critical points are "degenerate", i.e. the Hessian has some zero eigenvalues which as we saw above results from some eigenvalues of the Hamiltonian being degenerate (λ sense), and/or if some critical points are non-isolated which also will result when the Hessian has zero eigenvalues with non-radial eigenvectors (the critical "point" then becoming a line, or a linear manifold of dim = degeneracy of that λ). The case of an H with no λ-degeneracies is free of these difficulties and will be examined here.

The topological invariants of the closed and compact $(n-1)$ surface in V_n are the n Betti numbers, B_i. They may be calculated from the numbers of independent 0, 1, 2, ... $(n-1)$ simplexes as done in [10]. The $\{B_i\}$ are independent of any particular triangulation of the surface as they are topological invariants. For the $(n-1)$ sphere

$$B_0 = 1; \{B_1, B_2, \ldots, B_{n-2}\} = 0; B_{n-1} = 1. \tag{14}$$

[For the 2-sphere in ε_3 for example [10], $B_0 = 1$; $B_1 = r - f + 1$; $B_2 = 1$ where $r =$ no. of independent rings on any connected graph drawn on the sphere; $f =$ no. of faces (2-simplexes) so that if we draw e.g. a circle in the sphere, $r = 1$ and $f = 2$ yielding $B_1 = 0$.]

A "Morse number" M_i is the number of critical points of index i, i.e. $i = \eta_- =$ no. of the negative eigenvalues of the Hessian at that critical point.

The weak Morse inequalities are

$$M_i \geq B_i. \tag{15}$$

The strong inequalities are

$$\begin{aligned} &M_0 \geq B_0 \\ &M_1 - M_0 \geq B_1 - B_0 \\ &M_2 - M_1 + M_0 \geq B_2 - B_1 + B_0 \\ &M_{n-1} - M_{n-2} + \cdots + (-1)^{n-1} M_0 \geq B_{n-1} - B_{n-2} + \cdots + (-1)^{n-1} B_0. \end{aligned} \tag{16}$$

In general the last one becomes an equality.

We now examine the critical points we have found for $E[u]$ with an H of non-degenerate eigenvalues vis-a-vis Eqs. (16). The vectors $|u\rangle \in V_n$ and variations are on the $(n-1)$-unit sphere.

For concreteness let us take Dim $V_n = 5$ so that we have e.g. a 5×5 configuration-interaction problem, or a five pi-orbital MO problem.

The last of Eqs. (16) is an equality:

$$\begin{aligned} M_4 - M_3 + M_2 - M_1 + M_0 &= B_4 - B_3 + B_2 - B_1 + B_0 \\ &= 1 - 0 + 0 - 0 + 1 = 2. \end{aligned} \tag{17}$$

If we assumed from the previous section that for each of the five $\lambda^{(k)}$ there is one critical point, then M_3 through M_0 in Eq. (17) would cancel out yielding $M_4 = 2$, i.e. two maxima, a seeming contradiction with only one maximum one thought there were for the topmost eigenvalue at $|u^{(5)}\rangle$. Actually the $M_4 = 2$ is the correct and more complete number of maxima as given by the Morse theory. The seeming contradiction between the local theory ($\#\max = 1$) and the global Morse theory ($M_4 = \#\max = 2$) is resolved in the next two paragraphs. We note that actually as $|u\rangle$ (or $\boldsymbol{c}$) wanders on the unit-sphere $E[u]$ becomes a minimum, saddle point, or maximum on two points for each $\lambda^{(k)}$ on the surface of the unit sphere. Each eigenvector $|u^{(k)}\rangle$ direction defines a line through the center of the sphere which pierces the surface of the sphere once at the point $\boldsymbol{c}^{(k)} (\sum_i (c_i^{(k)})^2 = 1)$ and again at the diametrically opposite point $-\boldsymbol{c}^{(k)}$. Both points of the sphere satisfy the $\boldsymbol{v} = 0$ condition $[(\boldsymbol{H} - \lambda \boldsymbol{I})\boldsymbol{c} = 0]$ of the vector field. *Thus for each non-degenerate eigenvalue $\lambda^{(k)}$ of the Hamiltonian there are two critical points on the $(n-1)$-unit sphere.* This demonstrates how the topology of the compact variety on which the variables wander affects the number of critical points of a function of those variables.

The lower inequalities of Eq. (16) give

$$\# \text{ minima} = M_0 \geq 1$$

actually we have $M_0 = 2$.

$$\# \text{ saddle points of index } 1 = M_1$$

$$M_1 - M_0 \geq -1$$

or for $M_0 = 2$, $M_1 \geq 1$, actually $M_1 = 2$.

$$M_2 - M_1 + M_0 \geq 1$$

$$M_2 \geq (M_1 - M_0) + 1$$

in which with $M_1 = M_0 = 2$, $M_2 \geq 1$ actually $M_2 = 2$.

$$M_3 - M_2 + M_1 - M_0 \geq -1$$

or with $M_2 = M_1 = M_0 = 2$, $M_3 \geq 1$ actually $M_3 = 2$. Finally Eq. (17) which gave $\#$ of maxima $= M_4 = 2$.

The above example shows that the Morse relations are not sufficient to determine all of the numbers of critical points on the unit sphere. This is not surprising as the hypersphere has a very simple topology. Most of its Betti numbers are zero. Had the surface been a torus of some genus $g > 0$, more information would feed into the inequalities. Nevertheless the topological-variational relations give insight into the problem and narrow down the possible numbers of critical points, even determining some of them. They provide a useful check and guide globally while the Hessian acts locally.

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