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# Symmetry breaking for molecular open systems

by

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ABSTRACT. — We study the modifications to the energy levels of a molecule due to its interaction with an external boson (phonon or photon) reservoir. In the Hartree approximation it is shown that this leads to a non-linear functional, whose stationary states may break the symmetries of the isolated molecular Hamiltonian. These symmetries may often be restored by use of the generator coordinate method, which amounts to dressing the molecule with its boson cloud. The significance of these constructions for recent discussions of molecular structure is discussed.

## § 1. INTRODUCTION

In spite of several recent articles on the « problem of molecular structure » by Essen [7], Woolley [27] [28], Primas [22], Pfeifer [19] [20], Bader *et al.* [1] and others, there remain substantial disagreements about what would constitute a satisfactory solution. One general point of agreement, however, is that it is important to investigate the stability of molecules with respect to their interactions with the external environment. In order to assist future discussions of the problem, we thought that it would be useful to study a simple model of a molecule interacting with its environment for which substantial rigorous analysis is possible.

We consider the case where the environment is a free boson reservoir (phonons or photons), but allow the interaction to be as general as possible, in order to demonstrate the stability of the states obtained most convincingly. While our results and methods are a development of those of Davies [2] [3] and Pfeifer [19], the analysis presented here is more

satisfactory in several ways. Moreover the systematic use of group theory allows a much deeper understanding of the relationship between the use of the Hartree method and the symmetry breaking which occurs. We comment in passing that our results may be regarded as an application to quantum mechanics of general ideas concerning bifurcation and symmetry breaking reviewed by Sattinger in [*24*].

Our starting point is the Hamiltonian

$$H = H_0 + H_1 + F \tag{1.1}$$

on $\mathscr{H} \otimes \mathscr{F}$, where $\mathscr{H}$ is the Hilbert space associated with the molecule, or some subspace generated by specified eigenvectors of the molecular Hamiltonian $H_0$, which we assume to be self-adjoint and bounded below. The boson Fock space $\mathscr{F}$ has single particle space $\mathscr{F}_1$, and the reservoir Hamiltonian F is the free Hamiltonian whose single particle term $F_1$ is assumed to be self-adjoint, and strictly positive in the sense that

$$\langle F_1\phi, \phi \rangle > 0$$

for all non-zero $\phi$ in $\mathrm{Dom}\,(F_1) \subseteq \mathscr{F}_1$. Then the self-adjoint operator $F_1^{\lambda}$ has dense domain in $\mathscr{F}_1$ for all $\lambda \in \mathbb{R}$.

We shall assume that the interaction is of the form

$$H_1 = \sum_{r=1}^{n} \{ A_r a^*(f_r) + A_r^* a(f_r) \} \tag{1.2}$$

where $A_r$ are bounded operators on $\mathscr{H}$ and $a^*(f_r)$ are smeared field operators on $\mathscr{F}$. Somewhat more complicated interactions of the same general type could also be treated by our method. The starting point of our analysis is the following lemma.

LEMMA 1. — If $\| F_1^{-1/2} f_r \| < \infty$ for all $r$ then $H_1$ has form bound zero with respect to $H_0 + F$, so the self-adjoint operator H is well defined by (1.1) interpreted as a form sum, with

$$\mathrm{Quad}\,(H) = \mathrm{Quad}\,(H_0 + F) = \mathrm{Quad}\,(H_0) \cap \mathrm{Quad}\,(F).$$

*Proof.* — The basic computation is

$$\begin{aligned} \langle H_1\phi, \phi \rangle &\leqslant 2 \sum_{r=1}^{n} \| A_r\phi \| \, \| a(f_r)\phi \| \\ &\leqslant \sum_{r=1}^{n} \| A_r \| \{ \varepsilon \| a(f_r)\phi \|^2 + \varepsilon^{-1} \| \phi \|^2 \} \\ &= \sum_{r=1}^{n} \| A_r \| \langle a^*(f_r)a(f_r)\phi, \phi \rangle + a_\varepsilon \langle \phi, \phi \rangle . \end{aligned}$$

Now

$$|| F_1^{-1/2} f_r || = c_r < \infty$$

implies that

$$| F_1^{-1/2} f_r \rangle \langle F_1^{-1/2} f_r | \leqslant c_r^2 1$$

so

$$| f_r \rangle \langle f_r | \leqslant c_r^2 F_1$$

and

$$a^*(f_r) a(f_r) \leqslant c_r^2 F .$$

Thus

$$\langle H_1 \phi, \phi \rangle \leqslant \varepsilon \sum_{r=1}^{n} || A_r || c_r^2 \langle F\phi, \phi \rangle + a_\varepsilon \langle \phi, \phi \rangle .$$

The lemma now follows by application of standard quadratic form techniques [4] [23].

*Note.* — If we wanted $H_1$ to have operator bound less than one with respect to $H_0 + F$, or more weakly wanted H and $H_0 + F$ to have the same domain we would need to know that $\phi \otimes \Omega \in \text{Dom}\,(H_1)$ for all $\phi \in \text{Dom}\,(H_0)$, where $\Omega$ is the vacuum state. This happens if $\Omega$ lies in Dom $\{ a^*(f_r) \}$ for all $r$, which implies $|| f_r || < \infty$. The conditions $|| f_r || < \infty$ and $|| F_1^{-1/2} f_r || < \infty$ are not directly related.

Assuming $|| F_1^{-1/2} f_r || < \infty$ one can rearrange the sum in (1.2) so that (1.3) below holds. We shall henceforth assume that this has been done.

LEMMA 2. — If

$$\langle F_1^{-1} f_r, f_s \rangle = \delta_{rs} \tag{1.3}$$

then H is bounded below with

$$H \geqslant H_0 - \sum_{r=1}^{n} A_r^* A_r .$$

*Proof.* — From

$$\sum_{r=1}^{n} | F_1^{-1/2} f_r \rangle \langle F_1^{-1/2} f_r | \leqslant 1$$

we deduce

$$\sum_{r=1}^{n} | f_r \rangle \langle f_r | < F_1$$

and hence

$$\sum_{r=1}^{n} a^*(f_r) a(f_r) \leqslant F .$$

Hence

$$H \geqslant H_0 + \sum_{r=1}^{n} \{ a^*(f_r)a(f_r) + A_r a^*(f_r) + A_r^* a(f_r) \} = H_0 - \sum_{r=1}^{n} A_r^* A_r$$
$$+ \sum_{r=1}^{n} (a(f_r) + A_r)^*(a(f_r) + A_r) \geqslant H_0 - \sum_{r=1}^{n} A_r^* A_r .$$

We next use the Hartree method to obtain an upper bound on the infimum of the spectrum of H (that is on the ground state energy if there is a ground state). We do the Hartree minimisation in two stages.

LEMMA 3. — If we define

$$\mathscr{E}(\phi) = \inf \{ \langle H\phi \otimes \psi, \phi \otimes \psi \rangle : \| \psi \| = 1 \}$$

then

$$\mathscr{E}(\phi) = \langle H_0\phi, \phi \rangle - \sum_{r=1}^{n} | \langle A_r\phi, \phi \rangle |^2 .$$

*Proof.* — If $\psi \in \mathscr{F}_1$, the (Glauber) coherent state $\tilde{\psi} \in \mathscr{F}$ is defined by

$$\tilde{\psi} = e^{-\|\psi\|^2} \sum_{n=0}^{\infty} \frac{\otimes^n \psi}{\sqrt{n!}}$$

and satisfies the following well-known identities

$$\langle \tilde{\phi}, \tilde{\psi} \rangle = \exp \left\{ \langle \phi, \psi \rangle - \frac{1}{2} \| \phi \|^2 - \frac{1}{2} \| \psi \|^2 \right\}$$
$$a(f)\tilde{\psi} = \langle \psi, f \rangle \tilde{\psi}$$
$$\langle F\tilde{\phi}, \tilde{\psi} \rangle = \langle F_1\phi, \psi \rangle \langle \tilde{\phi}, \tilde{\psi} \rangle .$$

Now the operator $H_\phi$ on $\mathscr{F}$ defined by

$$\langle H_\phi\psi, \psi \rangle = \langle H\phi \otimes \psi, \phi \otimes \psi \rangle$$

is quadratic in the creation and annihilation operators, so

$$\mathscr{E}(\phi) = \inf \{ H\phi \otimes \tilde{\psi}, \phi \otimes \tilde{\psi} : \psi \in \mathscr{F}_1 \} .$$

If we put

$$g = \sum_{r=1}^{n} \langle A_r\phi, \phi \rangle f_r$$

then

$$\begin{aligned}\langle H\phi \otimes \tilde{\psi}, \phi \otimes \tilde{\psi} \rangle &= \langle H_0\phi, \phi \rangle + \langle F_1\psi, \psi \rangle \\ &\quad + \sum_{r=1}^{n} \{ \langle A_r\phi, \phi \rangle \langle f_r, \psi \rangle + \langle A_r^*\phi, \phi \rangle \langle \psi, f_r \rangle \} \\ &= \langle H_0\phi, \phi \rangle + \langle F_1\psi, \psi \rangle + \langle g, \psi \rangle + \langle \psi, g \rangle \\ &= \langle H_0\phi, \phi \rangle + \| F_1^{1/2}\psi + F_1^{-1/2}g \|^2 - \| F_1^{-1/2}g \|^2 \\ &\geqslant \langle H_0\phi, \phi \rangle - \| F_1^{-1/2}g \|^2 \\ &= \langle H_0\phi, \phi \rangle - \sum_{r=1}^{n} | \langle A_r\phi, \phi \rangle |^2\end{aligned}$$

so the infimum is as stated. For fixed $\phi$, the infimum is achieved, and the associated Hamiltonian $H_\phi$ on $\mathscr{F}$ does possess a ground state, if and only if $\psi = -F_1^{-1}g$ has finite norm, that is

$$\left\| \sum_{r=1}^{n} \langle A_r\phi, \phi \rangle F_1^{-1} f_r \right\| < \infty .$$

The condition that

$$\| F_1^{-1} f_r \| = \infty$$

for all $r$ is an extra infra-red condition on the interaction to which Pfeifer [*19*] attaches great importance. If it holds then one expects the Hamiltonian H to have no ground state within the Fock sector although it is bounded below. The physical explanation is that the molecule acquires a cloud of « soft » bosons of infinite number but finite total energy. It is then likely that the ground states of H are degenerate and associated with inequivalent representations of the commutation relations by means of some superselection rule which may be interpreted as a classical observable. In Section 5 we discuss Pfeifer's claim [*19*] [*20*] that this phenomenon actually occurs for a realistic model of a molecule interacting with the quantised electromagnetic field. We also note that Davies [*2*] gives a similar explanation for the existence of semi-classical solitary wave solutions of a certain non-linear Schrodinger equation.

We thus see that the Hartree method leads one to an analysis of the functional

$$\mathscr{E}(\phi) = \langle H_0\phi, \phi \rangle - \sum_{r=1}^{n} | \langle A_r\phi, \phi \rangle |^2 \qquad (1.4)$$

whose domain is the set of $\phi \in \mathscr{H}$ with $\| \phi \| = 1$ which lie in Quad $(H_0)$. This is actually the restriction to pure states of the functional

$$\mathscr{E}(\rho) = \text{tr } [H_0\rho] - \sum_{r=1}^{n} | \text{ tr } [A_r\rho] |^2 \tag{1.5}$$

whose domain may be taken to be

$$X = \{ \rho \geqslant 0 : \text{tr } [\rho] = 1 \}$$

if we allow $\mathscr{E}(\rho)$ to take the values $+\infty$ for certain mixed states $\rho$. Since the non-linear term in (1.5) is continuous and concave, the functional $\mathscr{E}$ on X is lower semicontinuous and concave. Other functionals of this general type have already been studied in [2] [3] [5] [13].

It is clear that the determination of the minima of $\mathscr{E}(\phi)$ is equivalent to the determination of the minima of $\langle H\xi, \xi \rangle$ for Hartree states $\xi = \phi \otimes \psi$. While the solution of this problem in interesting for its own sake, it may also be regarded as a first step towards the determination of the true ground state (or states) of H.

If $\dim \mathscr{H} < \infty$ then since $\mathscr{E}$ is continuous on the compact set of unit vectors in $\mathscr{H}$, it does have a minimum. A less trivial criterion, which is applicable to any molecule confined to a finite box, is as follows.

THEOREM 4. — If $(H_0 + i)^{-1}$ is a compact operator then the functional defined on the set of unit vectors in Quad $(H_0)$ by (1.4) does achieve its minimum value.

*Proof.* — By adding a constant we may assume that $H_0 \geqslant 0$. Let

$$c = \inf \{ \mathscr{E}(\phi) : \| \phi \| = 1 \}$$

and let $\phi_m \in \mathscr{H}$ be a sequence with $\| \phi_m \| = 1$ and $\mathscr{E}(\phi_m) \to c$. Since

$$| \mathscr{E}(\phi_m) - \langle H_0\phi_m, \phi_m \rangle | \leqslant \sum_{r=1}^{n} \| A_r \|^2$$

we see that $\langle H_0\phi_m, \phi_m \rangle$ is a bounded sequence. Thus $\| (H_0 + 1)^{1/2}\phi_m \|$ is a bounded sequence, and by the compactness of $(H_0 + 1)^{-1/2}$, $\{ \phi_m \}$ has a convergent subsequence, which we continue to label in the same way. If $\| \phi_m - \phi \| \to 0$ then

$$\lim_{m \to \infty} \langle A_r\phi_m, \phi_m \rangle = \langle A_r\phi, \phi \rangle$$

and

$$\liminf_{m \to \infty} \langle H_0\phi_m, \phi_m \rangle \geqslant \langle H_0\phi, \phi \rangle$$

by standard techniques [4] [23]. Hence

$$\mathscr{E}(\phi) \leqslant \liminf_{m \to \infty} \mathscr{E}(\phi_m) = c$$

so $\mathscr{E}(\phi) = c$.

Other criteria for the existence of a minimum to such functionals may be found in [2] [13].

It is clear from [2] [19] that one must not expect the minimum of $\mathscr{E}(\phi)$ to be unique. This non-uniqueness is a consequence of the use of the Hartree method, and a similar phenomenon occurs when one uses the Hartree-Fock method to analyse the electronic structure of a molecule in the fixed-nucleus approximation [8] [9] [14] [16]. Although the non-uniqueness is in one sense spurious, it does correspond to traditional ideas about molecular structure. For example in the Hartree-Fock analysis of the hydrogen molecule [8], the singularity discovered at $x = 2$ might be interpreted as a transition from a hydrogen molecule to two hydrogen atoms as the nuclei are separated adiabatically; in the exact solution, of course, this transition is not sharp. In the next section we shall apply the « generator coordinate method » [11] [26] [28] to the Hartree states obtained by the above procedure to find better approximations to the true ground state.

## § 2. GROUP SYMMETRIES

We next investigate the functional $\mathscr{E}(\phi)$ from the point of view of its group of symmetries. While we shall confine ourselves for simplicity to the case of a compact symmetry group $\mathscr{G}$, it is worth mentioning that the analysis of a similar functional in [2] depended crucially upon its invariance under the Euclidean group. In fact we shall be interested mainly in the cases where $\mathscr{G}$ is finite or $\mathscr{G} = \mathrm{SU}(2)$, the interpretation in the latter case being that it describes the rotational symmetry of the Hamiltonian.

We suppose that the compact group $\mathscr{G}$ has representations U and V on $\mathscr{H}$ and $\mathscr{F}$ respectively and that $\mathrm{H}_0$, $\mathrm{H}_1$ and F all commute with $\mathrm{U}_g \otimes \mathrm{V}_g$ for all $g \in \mathscr{G}$. It is then evident that

$$\mathscr{E}(\mathrm{U}_g\phi) = \mathscr{E}(\phi) \tag{2.1}$$

for all $\phi \in \mathscr{H}$ and $g \in \mathscr{G}$. We shall see that we have yet another variational problem where the minima break the symmetry of the functional being minimised [15] [24]. From (2.1) one may only deduce that if S is the set of unit vectors of $\phi \in \mathscr{H}$ at which $\mathscr{E}(\phi)$ takes its minimum then S is $\mathscr{G}$-invariant in the sense that $\phi \in \mathrm{S}$ implies $\mathrm{U}_g\phi \in \mathrm{S}$ for all $g \in \mathscr{G}$. Indeed the same applies to local minima or even stationary points of $\mathscr{E}$. If $\mathscr{G}$ is a compact Lie group then one obtains critical manifolds on which $\mathscr{E}$ is stationary.

It is tempting to identify the different isomeric forms associated with a given Hamiltonian, and the critical manifolds on which $\mathscr{E}$ has a local minimum. The different points on each manifold are then identified as different orientations of the chosen isomer. For the hydrogen molecule one expects the minimising manifold to coincide with the set of unoriented lines through the origin, while for a more complicated unsymmetrical

molecule a suitable manifold would be the set of all right-handed 3-frames. Application of the parity operator takes each manifold to a conjugate manifold, the two manifolds corresponding to stereoscopic isomers of the molecule.

We now suppose that $\dim \mathscr{H} < \infty$ and let $\tilde{\mathscr{H}}$ denote the complex space of linear operators on $\mathscr{H}$ with the inner product

$$\langle A, B \rangle = \mathrm{tr}\ [B^*A].$$

The representation U of $\mathscr{G}$ on $\mathscr{H}$ induces a representation $\tilde{U}$ on $\tilde{\mathscr{H}}$ by the formula

$$\tilde{U}_g(A) = U_g A U_g^*.$$

The following theorem provides a canonical form for the invariant functionals in which we are interested.

THEOREM 5. — Suppose that the functional $\mathscr{W}$ on $\tilde{\mathscr{H}}$ is given by

$$\mathscr{W}(\rho) = -\sum_{r=1}^{n} |\ \mathrm{tr}\ [A_r \rho]\ |^2$$

and is invariant in the sense that

$$\mathscr{W}(U_g \rho) = \mathscr{W}(\rho)$$

for all $\rho \in \tilde{\mathscr{H}}$ and $g \in \mathscr{G}$. Then $\mathscr{W}$ may be written as a linear combination with negative coefficients of functions of the form

$$\rho \to \langle \mathscr{P}\rho, \rho \rangle = \sum_{s=1} |\ \mathrm{tr}\ [B_s \rho]\ |^2$$

where $\{ B_s^* \}$ is an orthonormal basis within $\tilde{\mathscr{H}}$ of a linear subspace of $\tilde{\mathscr{H}}$ on which U acts irreducibly.

*Proof.* — There is a unique operator $\mathscr{A}$ on $\tilde{\mathscr{H}}$ such that

$$\langle \mathscr{A}\rho, \rho \rangle = \sum_{r=1}^{n} |\ \mathrm{tr}\ [A_r \rho]\ |^2$$

for all $\rho \in \tilde{\mathscr{H}}$, namely

$$\mathscr{A} = \sum_{r=1}^{n} |\ A_r^* \rangle \langle A_r^*\ |.$$

This operator is non-negative, self-adjoint, and commutes with $\tilde{U}_g$. Therefore it lies in the *-algebra $\mathscr{U}$ of all operators on $\tilde{\mathscr{H}}$ which commute with $\tilde{\mathscr{U}}_g$. We may write

$$\mathscr{A} = \Sigma \lambda_i \mathscr{P}_i$$

where $\lambda_i > 0$ and $\mathscr{P}_i$ are minimal projections in $\mathscr{U}$, that is projections onto irreducible subspaces for $\tilde{U}_g$. If $\{ B_s^* \}_s^m = 1$ is an orthonormal basis for one such subspace $\mathscr{P}\tilde{\mathscr{H}}$ then

$$\mathscr{P} = \sum_{s=1}^{m} | B_s^* \rangle \langle B_s^* |$$

so

$$\langle \mathscr{P}\rho, \rho \rangle = \sum_{s=1}^{m} | \text{tr } [B_s\rho] |^2$$

as stated.

*Note.* — We have chosen in the above theorem to work with the complex space $\tilde{\mathscr{H}}$ of all operators $\rho$ on $\mathscr{H}$. Of course $\tilde{\mathscr{U}}_g$ has the property

$$\tilde{U}_g(\rho^*) = (\tilde{U}_g\rho)^*$$

and we could have restricted to the real space of self-adjoint $\rho$ in $\tilde{\mathscr{H}}$. Correspondingly if $A_r = C_r + iD_r$ where $C_r = C_r^*$ and $D_r = D_r^*$ then

$$\mathscr{W}(\rho) = -\sum_{r=1}^{n} | \text{tr } [C_r\rho] |^2 - \sum_{r=1}^{n} | \text{tr } [D_r\rho] |^2$$

for all $\rho = \rho^*$. We leave the reader to formulate a real version of Theorem 5 with these hints.

We shall say that operators with the properties of $\{ B_s \}$ of Theorem 5 transform under $\mathscr{G}$ according to the relevant irreducible representation of G. Our next criterion for symmetry breaking generalises Theorem 3.2 of [2].

THEOREM 6. — Suppose that $\mathscr{E}$ is defined by

$$\mathscr{E}(\phi) = \langle H_0\phi, \phi \rangle - \alpha \sum_{r=1}^{n} | \langle A_r\phi, \phi \rangle |^2$$

where $\alpha > 0$, $H_0$ commutes with the representation U of $\mathscr{G}$, and $\{ A_r \}$ transform according to an irreducible representation V of $\mathscr{G}$ other than the trivial one-dimensional representation. Suppose also that the ground state of $H_0$ is unique (up to phase) with energy E. Then the minimum of $\mathscr{E}(\phi)$ is not unique if there exists a unit vector $\phi \in \mathscr{H}$ with

$$\mathscr{E}(\phi) < E. \tag{2.2}$$

*Proof.* — Suppose that the minimum of $\mathscr{E}$ is unique (apart from phases)

and is taken at the unit vector $\phi_0$. Then by the $\mathcal{G}$-invariance of $\mathcal{E}$ we have

$$U_g\phi_0 = e^{i\theta(g)}\phi_0$$

for all $g \in \mathcal{G}$. Hence

$$\begin{aligned} \langle A\phi_0, \phi_0 \rangle &= \langle AU_g^*\phi_0, U_g^*\phi_0 \rangle \\ &= \langle U_gAU_g^*\phi_0, \phi_0 \rangle \\ &= V_g \langle A\phi_0, \phi_0 \rangle . \end{aligned}$$

But the irreducible representation V on $\mathbb{C}^n$ is assumed to be different from the trivial one-dimensional representation so

$$\langle A_r\phi_0, \phi_0 \rangle = 0$$

for all $r$. Thus

$$\mathcal{E}(\phi_0) = \langle H_0\phi_0, \phi_0 \rangle \geqslant E$$

which contradicts (2.2).

In the following applications of the above theorems, $\pi_l$ denotes the irreducible representation of spin $l$ and dimension $(2l + 1)$ of the group SU(2).

THEOREM 7. — Let the functional $\mathcal{W}$ be invariant with respect to the irreducible representation $\pi_l$ of SU(2) on $\mathcal{H}$. Then

$$\mathcal{W}(\rho) = -\sum_{r=0}^{2l} \lambda_r \langle \mathcal{P}_r\rho, \rho \rangle$$

for all $\rho \in \tilde{\mathcal{H}}$, where $\lambda_r \geqslant 0$ and $\mathcal{P}_r$ is the projection of $\tilde{\mathcal{H}}$ onto the subspace associated with $\pi_r$ in the decomposition

$$\pi_l \otimes \pi_l = \pi_0 \oplus \pi_1 \ldots \oplus \pi_{2l}. \tag{2.3}$$

Moreover one has the explicit forms

$$\langle \mathcal{P}_0\rho, \rho \rangle = (2l + 1)^{-1/2} |\operatorname{tr} [\rho]|^2$$

$$\langle \mathcal{P}_1\rho, \rho \rangle = \left\{\frac{3}{l(l + 1)(2l + 1)}\right\}^{1/2} \sum_{i=1}^{3} |\operatorname{tr} [J_i]|^2.$$

THEOREM 8. — Let $\mathcal{W}$ be defined by

$$\mathcal{W}(\phi) = -\sum_{i=1}^{3} |\langle J_i\phi, \phi \rangle|^2$$

where $J_i$ are associated with the irreducible representation $\pi_l$ of SU(2) on $\mathcal{H}$. Then $\mathcal{W}$ is SU(2) invariant and satisfies

$$-l^2 \leqslant \mathcal{W}(\phi) \leqslant 0$$

for all $|| \phi || = 1$. Moreover $\mathscr{W}(\phi) = -l^2$ if and only if $\phi$ is a Bloch coherent state, so that

$$S = \{ \phi : || \phi || = 1 \quad \text{and} \quad \mathscr{W}(\phi) = -l^2 \}$$

is a compact 3-dimensional manifold.

*Proof.* — Given $\phi \in \mathscr{H}$ with $|| \phi || = 1$ the vector $v \in \mathbb{R}^3$ with components

$$v_i = \langle J_i \phi, \phi \rangle$$

may be rotated by application of some $g \in SU(2)$ until it lies along the $z$-axis. Then

$$\langle J_1 \pi_g \phi, \pi_g \phi \rangle = \langle J_2 \pi_g \phi, \pi_g \phi \rangle = 0$$

and

$$\langle J_3 \pi_g \phi, \pi_g \phi \rangle \geqslant 0$$

so that

$$\mathscr{W}(\phi) = \mathscr{W}(\pi_g \phi) = -\langle J_3 \pi_g \phi, \pi_g \phi \rangle^2 .$$

Hence $\mathscr{W}(\phi) \geqslant -l^2$ with equality if and only if $\pi_g \phi = e^{-i\theta} \phi_l$ where $\phi_l$ is the eigenvector of $J_3$ with eigenvalue $l$.

Thus

$$\phi = e^{i\theta} \pi_g^{-1} \phi_l$$

and $\phi$ is a Bloch coherent state, apart from a phase factor. For an explicit parametrisation of the Bloch coherent states see [*12*].

For the sake of completeness we describe once again an example of Pfeifer [*19*], which is relevant to the phenomenon of stereoisomerism. For unit vectors $\phi \in \mathbb{C}^2$ we put

$$\mathscr{E}(\phi) = \varepsilon \langle \sigma_1 \phi, \phi \rangle - \Lambda \langle \sigma_3 \phi, \phi \rangle^2$$

where $\varepsilon > 0$, $\Lambda > 0$ and

$$\sigma_1 = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \qquad \sigma_3 = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}.$$

The functional $\mathscr{E}$ is invariant with respect to the « parity » operator $\sigma_1$ which generates a unitary group of two elements. Elementary computations lead to the following result.

PROPOSITION 9. — If $\varepsilon \geqslant 2\Lambda$ then the functional $\mathscr{E}(\phi)$ takes its minimum value $-\varepsilon$ at the state $\phi = (2^{-1/2}, -2^{-1/2})$, which is unique, up to phases. If $\varepsilon < 2\Lambda$ then $\mathscr{E}(\phi)$ takes its minimum value $(-\Lambda - \varepsilon^2/4\Lambda)$ at $\phi = (\cos \theta, -\sin \theta)$ where $\theta$ is one of the two solutions of $\sin 2\theta = \varepsilon/2\Lambda$.

Note that if $\varepsilon < 2\Lambda$ the two solutions are permuted by the action of $\sigma_1$. Moreover if $\varepsilon \ll 2\Lambda$ then the two solutions are approximately (1, 0) and (0, 1). This situation, where the level splitting $2\varepsilon$ is negligible compared with the the effective strength $\Lambda$ of the interaction with the external environment, is precisely the one in which one expects stereoscopic isomers to be stable.

We commented at the end of Section 1 that the symmetry breaking discovered is a consequence of the use of the Hartree method. Let us now suppose in addition to (1.3) that $f_r$ satisfy

$$\| F_1^{-1} f_r \| < \infty$$

for all $r$, and that $\phi_0 \in \mathscr{H}$ is a unit vector which minimises $\mathscr{E}(\phi)$. Then the functional

$$\langle H\phi \otimes \tilde{\psi}, \phi \otimes \tilde{\psi} \rangle$$

achieves its minimum for $\phi = \phi_0$ and $\psi = \psi_0 \in \mathscr{F}_1$ where

$$\psi_0 = -\sum_{r=1}^{n} \langle A_r \phi_0, \phi_0 \rangle F_1^{-1} f_r .$$

We immediately see that the minimum is actually achieved at each of the points

$$\xi_g = U_g \phi_0 \otimes V_g \tilde{\psi}_0 = U_g \phi_0 \otimes (V_g \psi_0)^{\sim} .$$

The essence of the « generator coordinate method » as described in [11] [26] [28] is that one can obtain a better approximation to the true ground state of H by using « parametric wave functions » $f : \mathscr{G} \to \mathbb{C}$ to construct states $\eta_f \in \mathscr{H} \otimes \mathscr{F}$ according to the formula

$$\eta_f = \int_{\mathscr{G}} f(g) \xi_g dg . \tag{2.4}$$

In order that $\| \eta_f \| = 1$ the parametric wave function $f$ must satisfy the normalisation condition

$$\int_{\mathscr{G}} \int_{\mathscr{G}} f(g) \overline{f(h)} \langle \xi_g, \xi_h \rangle \, dg dh = 1 .$$

In many cases $f$ may be regarded as a function not on $\mathscr{G}$ but on a transitive $\mathscr{G}$-space, such as the unit sphere $S_2$ in $\mathbb{R}^3$ when $\mathscr{G} = SU(2)$. If $\| \psi_0 \|$ is large, or equivalently if the expected particle number of $\tilde{\psi}_0$ is large, then one may regard the states $\xi_g$ as more or less independent classical configurations of the molecule, since the kernel $\langle \xi_g, \xi_h \rangle$ is extremely small except for $g \fallingdotseq h$.

## § 3. ESTIMATES OF THE GROUND STATE ENERGY

Although it is plausible that one can obtain quite good estimates of the ground state energy by use of the generator coordinate method, it is difficult to prove general theorems about this. However, it is relevant

to note that Falicov and Harris [8] found that a symmetrisation of the unrestricted Hartree-Fock method considerably reduced the error in the computation of the electronic ground state energy for a simple exactly soluble model of the hydrogen molecule.

In this section we support our claim by treating two simple examples, the first of which is an abstraction of Pfeifer's model of stereoisomerism [19], also treated in Proposition 9 above.

The Hamiltonian of this model on $\mathbb{C}^2 \otimes \mathscr{F}$ is

$$H = \varepsilon\sigma_1 + F + \Lambda^{1/2}\sigma_3 \{ a(f) + a^*(f) \}$$

where

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

and

$$\langle F_1^{-1} f, f \rangle = 1 .$$

We wish to estimate the ground state energy E of H when the energy splitting $2\varepsilon$ of the system $\mathbb{C}^2$ is very small compared with $\Lambda$.

By Lemma 2 and Proposition 9 we find that

$$-\Lambda - \varepsilon \leqslant E \leqslant -\Lambda - \varepsilon^2/4\Lambda .$$

We shall show that the coefficient of $\varepsilon$ in both of these bounds is incorrect, under an extra condition which ensures that H does actually possess a ground state.

THEOREM 10. — If there exists a constant $\mu > 0$ such that $F_1 \geqslant \mu 1$ then the vector $\psi = -\Lambda^{1/2} F_1^{-1} f$ satisfies

$$N \equiv \| \psi \|^2 \leqslant \Lambda\mu^{-1} < \infty .$$

Moreover for small enough $\varepsilon > 0$ the Hamiltonian H possesses a non-degenerate ground state with energy

$$E = -\Lambda - \varepsilon e^{-2N} + 0(\varepsilon^2) .$$

*Proof.* — We consider H as a perturbation of the operator

$$K = F + \Lambda^{1/2}\sigma_3 \{ a(f) + a^*(f) \} = \begin{bmatrix} K_{11} & 0 \\ 0 & K_{22} \end{bmatrix}$$

where

$$K_{11} = F + \Lambda^{1/2} \{ a(f) + a^*(f) \}$$
$$K_{22} = F - \Lambda^{1/2} \{ a(f) + a^*(f) \} .$$

The operators K are unitarily equivalent to F, and have ground states $\tilde{\psi}$ and $(-\psi)^{\sim}$ respectively. The vector

$$\eta_1 = \begin{bmatrix} \tilde{\psi} \\ 0 \end{bmatrix}, \qquad \eta_2 = \begin{bmatrix} 0 \\ (-\psi)^{\sim} \end{bmatrix}$$

form an orthonormal basis for the eigenspace of K corresponding to the ground state eigenvalue $-\Lambda$, which is an isolated eigenvalue.

Now

$$\langle \sigma_1\eta_1, \eta_1 \rangle = \langle \sigma_1\eta_2, \eta_2 \rangle = 0$$
$$\langle \sigma_1\eta_1, \eta_2 \rangle = \langle \tilde{\psi}, (-\psi)^{\sim} \rangle = e^{-2N}.$$

It follows by perturbation theory that the eigenvalue $-\Lambda$ splits into two eigenvalues of multiplicity one for small $\varepsilon > 0$, and that these eigenvalues are analytic functions of $\varepsilon$ given by

$$E^{\pm}(\varepsilon) = -\Lambda \pm \varepsilon e^{-2N} + 0(\varepsilon^2). \tag{3.1}$$

We observe that the generator coordinate method also yields the formula (3.1) as an upper bound for the ground state energy. For the states $\eta_1$ and $\eta_2$ are clearly Hartree states, while the state which leads to (3.1) is the anti-symmetric combination

$$\eta = 2^{-1/2}(\eta_1 - \eta_2).$$

It may be checked that one obtains the same results if one uses not $\eta_1$ and $\eta_2$ but the Hartree states which yield the exact minimisation of

$$\langle H\phi \otimes \tilde{\psi}, \phi \otimes \tilde{\psi} \rangle.$$

Our second example is a development of the first, which for large $n$ provides a simplified model of the interactions between the rotational excitations of a planar molecule and the external environment. The fact that the rotational excitations of a typical molecule have much smaller energies than the vibrational or electronic excitations [*10*, p. 314] justifies treating them separately, and also makes it plausible that they will be strongly affected by even weak interactions with the environment.

We suppose that $\{ e_r \}_{r=1}^n$ is an orthonormal basis for $\mathscr{H}$ and that the corresponding wave-functions are distributed around a circle so that we can identify $e_r$ with $e_{n+r}$ for all integers $r$. We define the system Hamiltonian by

$$H_0 e_r = 2e_r - e_{r-1} - e_{r+1}.$$

LEMMA 11. — The Hamiltonian $H_0$ is non-negative with ground state energy 0 and

$$\text{tr } [H_0] = 2n.$$

Moreover the eigenvectors of $H_0$ are

$$u_s = n^{-1/2} \sum_{r=1}^{n} \omega^{rs} e_r$$

where

$$\omega = e^{2\pi i/n}.$$

*Proof.* — This elementary computation may be regarded as taking

Fourier transforms with respect to the symmetry group $\mathcal{G} = \mathbb{Z}_n$ of the Hamiltonian. If

$$Ue_r = e_{r+1} \tag{3.2}$$

then $U^n = 1$, U commutes with $H_0$ and $u_s$ are the eigenvectors of U. Moreover

$$H_0 = 2 - U - U^* .$$

Now let the operator E on $\mathcal{H}$ be defined by

$$Ee_r = \omega^r e_r$$

so that

$$U^*EU = \omega E .$$

Also let F be the usual quadratic Hamiltonian on $\mathcal{F}$ and let V be a unitary operator on $\mathcal{F}$ such that $V^n = 1$, V commutes with F, and

$$Va^*(h)V^* = a^*(V_1 h)$$

for all $h$, where $V_1$ is the restriction of V to the one-particle space, which we suppose to be invariant. Finally let $f, g$ be single-particle wave-functions such that

$$\langle F_1^{-1} f, f \rangle = \langle F_1^{-1} g, g \rangle = 1 \tag{3.3}$$

$$\langle F_1^{-1} f, g \rangle = 0 \tag{3.4}$$

$$\| F_1^{-1} f \|^2 = \| F_1^{-1} g \|^2 \equiv \mu < \infty . \tag{3.5}$$

LEMMA 12. — If $\varepsilon, \lambda > 0$ and

$$H = \varepsilon H_0 + F + \lambda H_1$$

where

$$H_1 = \{ Ea^*(f) + E^* a(f) \} + \{ E^* a^*(g) + Ea(g) \}$$

then H commutes with $U \otimes V$ if and only if

$$V_1 f = \omega f, \qquad V_1 g = \omega^{-1} g . \tag{3.6}$$

*Proof.* — This is an elementary computation.

LEMMA 13. — The ground state energy E of H satisfies

$$-2\lambda^2 \leqslant E \leqslant -2\lambda^2 + 2\varepsilon .$$

*Proof.* — It follows from Lemma 2 that

$$\begin{aligned} H &\geqslant \varepsilon H_0 - \lambda^2 (E^* E + E E^*) \\ &= \varepsilon H_0 - 2\lambda^2 \\ &\geqslant -2\lambda^2 . \end{aligned}$$

On the other hand Lemma 3 implies that

$$\begin{aligned} \mathcal{E}(e_r) &= \varepsilon \langle H_0 e_r, e_r \rangle - \lambda^2 | \langle Ee_r, e_r \rangle |^2 - \lambda^2 | \langle E^* e_r, e_r \rangle |^2 \\ &= 2\varepsilon - 2\lambda^2 . \end{aligned}$$

We now suppose that $\varepsilon > 0$ is very small, and see from the above that the states $e_r$ come close to minimising the functional $\mathscr{E}(\phi)$. By the proof of Lemma 3 the corresponding Hartree states are

$$\phi_r = e_r \otimes \tilde{\psi}_r$$

where

$$\psi_r = -\lambda F_1^{-1} \{ \omega^r f + \omega^{-r} g \}. \tag{3.7}$$

The map from the orthonormal set $e_r \otimes \Omega$ to the orthonormal set $\phi_r$ is an example of a dressing transformation.

THEOREM 14. — The ground state of $F + \lambda H_1$ is $n$-fold degenerate with basis $\{ \phi_r \}_{r=1}^n$ and energy $(-2\lambda^2)$. Moreover $F + \lambda H_1$ commutes with $U \otimes V$ and

$$(U \otimes V)\phi_r = \phi_{r+1}. \tag{3.8}$$

*Proof.* — The Hamiltonian leaves each subspace $e_r \otimes \mathscr{F}$ invariant and within that subspace equals

$$F + \lambda \{ \omega^r a^*(f) + \omega^{-r} a(f) + \omega^{-r} a^*(g) + \omega^r a(g) \}$$
$$= F + a^* \{ \lambda \omega^r f + \lambda \omega^{-r} g \} + a \{ \lambda \omega^r f + \lambda \omega^{-r} g \}$$

whose ground state is $\psi_r$. The identity (3.8) is proved using (3.2) and (3.6).

In order to apply perturbation theory we need to assume that the ground state energy $(-2\lambda^2)$ of $F + \lambda H_1$ is an isolated eigenvalue. We therefore assume that there exists a constant $\nu > 0$ such that

$$F_1 \geqslant \nu 1. \tag{3.9}$$

THEOREM 15. — If (3.9) holds and $\varepsilon > 0$ is sufficiently small then the ground state of

$$H = \varepsilon H_0 + F + \lambda H_1$$

is non-degenerate and has energy

$$E = -2\lambda^2 + 2(1 - \gamma)\varepsilon + 0(\varepsilon^2) \tag{3.10}$$

where

$$\gamma = \exp\left[ 2\lambda^2 \mu \left\{ \cos \frac{2\pi}{n} - 1 \right\} \right]. \tag{3.11}$$

Moreover the ground state of H is the symmetrised Hartree state

$$\psi = n^{-1/2} \{ \phi_1 + \ldots + \phi_n \} + 0(\varepsilon). \tag{3.12}$$

*Proof.* — This depends upon calculating

$$\langle H_0 \phi_r, \phi_s \rangle = \langle H_0 e_r, e_s \rangle \langle \tilde{\psi}_r, \tilde{\psi}_s \rangle.$$

This vanishes if $|r-s|>1$ and equals 2 if $r=s$.
If $|r-s|=1$ then

$$\begin{aligned}\langle H_0\phi_r, \phi_s\rangle &= -\exp\left\{\langle \psi_r, \psi_s\rangle - \frac{1}{2}\|\psi_r\|^2 - \frac{1}{2}\|\psi_s\|^2\right\}\\ &= -\exp\left[\lambda^2\mu(\omega+\omega^{-1}-2)\right]\\ &= -\gamma\end{aligned}$$

by (3.3) (3.4) (3.5) and (3.7). The formulae (3.10) and (3.12) are now routine applications of perturbation theory.

By comparing (2.4) and (3.12) we see that to the lowest order in perturbation theory the ground state of H is indeed given by the generator coordinate method, the symmetry group being $\mathcal{G}=\mathbb{Z}_n$. Further calculations along the above lines show that the gap between the bottom $n$ energy levels of H is reduced by the factor $\gamma$ compared with the gap between the $n$ energy levels of $\varepsilon H_0$, a result which may be interpreted as a mass renormalisation associated with the dressing transformation. From (3.11) we see that

$$0<\gamma<1$$

and that $\gamma$ is very small if the number $\mu$, which is proportional to the number of field particles in the ground state, is very large. The indications are that if $\mu=\infty$ then the Hamiltonian H is bounded below and its ground state is $n$-fold degenerate, each ground state vector being associated with an inequivalent representation of the CCR's.

## § 4. CRITICAL POINTS OF $\mathcal{E}(\phi)$

As well as the absolute minimum of $\mathcal{E}(\phi)$, one is interested in the existence of local minima, which may correspond to structural isomers of high stability. In this section we present a method of determining such local minima, and indeed all critical points. For simplicity we suppose that

$$\mathcal{E}(\phi)=\langle H_0\phi, \phi\rangle - \alpha\sum_{r=1}^{n}|\langle A_r\phi, \phi\rangle|^2$$

where $\alpha>0$, the Hilbert space $\mathcal{H}$ is finite-dimensional and $\phi$ lies in the set S of unit vectors in $\mathcal{H}$.

THEOREM 16. — The element $\phi$ of S is a critical point of $\mathcal{E}$ if and only if $\phi$ is an eigenvector of

$$H=H_0-\sum_{r=1}^{n}(\bar{\lambda}_r A_r+\lambda_r A_r^*)$$

where the parameters $\lambda_r$ satisfy the consistency conditions

$$\lambda_r = \alpha \langle A_r\phi, \phi \rangle .$$

*Proof.* — This is a modification of Theorem 2.4 of [2]. The vector $\phi \in S$ is a critical point if and only if

$$\frac{\partial}{\partial\theta} \{ \phi \cos \phi + \psi \sin \theta \} |_{\theta=0} = 0$$

for all $\psi \in S$ such that $\langle \phi, \psi \rangle = 0$. Thus

$$\begin{aligned} 0 &= \langle H_0\psi, \phi \rangle + \langle H_0\phi, \psi \rangle \\ &\quad - \alpha \sum_{r=1}^{n} \overline{\langle A_r\phi, \phi \rangle} \{ \langle A_r\psi, \phi \rangle + \langle A_r\phi, \psi \rangle \} \\ &\quad - \alpha \sum_{r=1}^{n} \langle A_r\phi, \phi \rangle \{ \langle \psi, A_r\phi \rangle + \langle \phi, A_r\psi \rangle \} \\ &= \langle \psi, g \rangle + \langle g, \psi \rangle \end{aligned} \tag{4.1}$$

where

$$g = H_0\phi - \alpha \sum_{r=1}^{n} \{ \bar{\lambda}_r A_r\phi + \lambda_r A_r^*\phi \} .$$

The equality (4.1) can only hold for all $\psi$ of the stated type if $g$ is a multiple of $\phi$.

As a first illustration of the above theorem we reconsider the functional $\mathscr{W}$ defined in Theorem 8. The critical manifolds obtained in the following theorem are manifolds of SU(2) coherent states as introduced by Perelomov [17]. It is surely possible to extend the theorem to more general compact Lie groups; see [6] [18] [25] and other references cited there for closely related results.

THEOREM 17. — The critical manifolds of $\mathscr{W}$ are in one-one correspondence with the values 0 and

$$\{ -(l-r)^2 : r = 0, 1, 2, \ldots \text{ and } r < l \} .$$

The values 0 and $-l^2$ correspond to the global maximum and minimum respectively, while the other values correspond to degenerate saddle points.

*Proof.* — The problem is to find solutions $\phi \in S$ of the pair of equations

$$-\sum_{r=1}^{3} \lambda_r J_r \phi = E\phi \tag{4.2}$$

$$\lambda_r = \langle J_r\phi, \phi \rangle .$$

The possibility $\lambda_1 = \lambda_2 = \lambda_3 = 0$ actually occurs and maximises $\mathscr{W}$. Assuming $\lambda_r$ do not all vanish then by rotating coordinates we may assume that $\lambda_1 = \lambda_2 = 0$ and $\lambda_3 > 0$, so that (4.2) becomes

$$-\lambda_3 J_3 \phi = E\phi .$$

Thus $\phi$ must equal one of eigenvectors of $J_3$, and by the condition $\lambda_3 > 0$ we have

$$J_3\phi = (l - r)\phi$$

where $r = 0, 1, 2, \ldots$ and $r > l$. It is a trivial matter to check that these eigenvectors, which are unique up to phases, do satisfy the consistency conditions $\lambda_1 = \lambda_2 = 0$. The critical manifolds arise from these orientated solutions by applying the group SU(2).

It remains to prove that if

$$0 < m = l - r < l$$

then a point $\phi$ on the critical manifold is a degenerate saddle point. The degeneracy is an obvious consequence of the fact that $\mathscr{W}$ is constant on each critical manifold. If

$$J_3\phi_m = m\phi_m , \qquad J_3\phi_{\pm l} = \pm l\phi_{\pm l}$$

and

$$\psi_\theta = \phi_m \cos\theta + \phi_l \sin\theta$$

then

$$\begin{aligned} \mathscr{W}(\psi_\theta) &\leqslant -\langle J_3\psi_\theta, \psi_\theta \rangle^2 \\ &= -\{ m\cos^2\theta + l\sin^2\theta \}^2 < -m^2 \end{aligned}$$

for $\theta \neq 0$, so $\phi_m$ is not a local minimum. On the other hand if

$$\psi_\theta = \phi_m \cos\theta + \phi_{-l} \sin\theta$$

then

$$\begin{aligned} \mathscr{W}(\psi_\theta) &= -\langle J_3\psi_\theta, \psi_\theta \rangle^2 \\ &= -\{ m\cos^2\theta - l\sin^2\theta \}^2 = -m^2 + 2m(l+m)\theta^2 + 0(\theta^4) \end{aligned}$$

so $\phi_m$ is not a local maximum either.

The above theorem describes to a first approximation the effect of the non-linear term $\mathscr{W}$ on a discrete energy level of a Hamiltonian when the relevant eigenspace carries an irreducible representation of SU(2). We now give a deeper analysis of this problem.

We suppose that H is a self-adjoint operator on the finite-dimensional Hilbert space $\mathscr{H}$ and that E is an isolated eigenvalue of $H_0$ whose corresponding eigenspace $\mathscr{K}$ has dimension $(2l + 1)$. We suppose that $H_0$ commutes with a representation U of SU(2) and that the restriction of U to $\mathscr{K}$ is the irreducible representation $\pi_l$. We also suppose that $A_1$, $A_2$, $A_3$ are three bounded self-adjoint operators on $\mathscr{H}$ which transform according to the representation $\pi_1$. That is if $v \in \mathbb{R}^3$ then

$$U_g(v \cdot A)U_g^* = (\pi_1^g v) \cdot A \tag{4.3}$$

If P is the projection of $\mathscr{H}$ onto $\mathscr{K}$ then the restrictions $PA_iP$ of $A_i$ to $\mathscr{K}$ also transform according to $\pi_1$ so

$$PA_iP = \beta J_i$$

by (2.3). We consider only the generic case $\beta \neq 0$ and define the functional $\mathscr{E}$ by

$$\mathscr{E}(\phi) = \langle H_0\phi, \phi \rangle - \alpha \sum_{r=1}^{3} \langle A_i\phi, \phi \rangle^2$$

where $\alpha > 0$ and $\phi \in S$.

THEOREM 18. — For small enough $\alpha > 0$ the functional $\mathscr{E}$ possesses critical manifolds which are small perturbations of the critical manifolds within $\mathscr{K}$ as determined in Theorem 17.

*Proof.* — We start by decomposing $\mathscr{H}$ as the direct sum of $\mathscr{H}_m$ where

$$\mathscr{H}_m = \{ \phi \in \mathscr{H} : J_3\phi = m\phi \}.$$

If $m = l - r$ where $r = 0, 1, 2, \ldots$ and $r < l$ then $\mathscr{H}_m \cap \mathscr{K}$ is one-dimensional. If $\phi \in \mathscr{H}_m$ for such a value of $m$ then

$$\begin{aligned} \langle A_1\phi, \phi \rangle &= \langle A_1 e^{im\theta}\phi, e^{im\theta}\phi \rangle \\ &= \langle e^{-iJ_3\theta}A_1 e^{iJ_3\theta}\phi, \phi \rangle = \langle (A_1 \cos 2\theta + A_2 \sin 2\theta)\phi, \phi \rangle \end{aligned}$$

by (4.3). Since $\theta \in \mathbb{R}$ is arbitrary we deduce that

$$\langle A_1\phi, \phi \rangle = \langle A_2\phi, \phi \rangle = 0.$$

Our problem is to find $\phi \in \mathscr{H}_m \cap S$ satisfying the pair of equations

$$\begin{aligned} (H_0 - \lambda A_3)\phi &= \gamma\phi \\ \alpha \langle A_3\phi, \phi \rangle &= \lambda. \end{aligned}$$

Now withim $\mathscr{H}_m$, E is an isolated eigenvalue of H with multiplicity one and eigenvector $\phi_m$ say. Analytic perturbation theory implies that for small enough real $\lambda$ there exist a normalised eigenvector $\phi(\lambda)$ and eigenvalue $\gamma(\lambda)$ of $(H_0 - \lambda A_3)$ which are analytic functions of $\lambda$ and satisfy

$$\begin{aligned} (H_0 - \lambda A_3)\phi(\lambda) &= \gamma(\lambda)\phi(\lambda) \\ \phi(0) = \phi_m, \quad \gamma(0) &= E. \end{aligned}$$

Then $\langle A_3\phi(\lambda), \phi(\lambda)\rangle$ is an analytic function of $\lambda$ such that

$$\langle A_3\phi(0), \phi(0)\rangle = \langle A_3\phi_m, \phi_m\rangle = \langle \beta J_3\phi_m, \phi_m\rangle = \beta m \neq 0,$$

so $\langle A_3\phi(\lambda), \phi(\lambda)\rangle$ is non-zero for small enough $\lambda \neq 0$. It follows that

$$\alpha \langle A_3\phi(\lambda), \phi(\lambda)\rangle = \lambda$$

can be solved to express $\lambda$ as an analytic function of $\alpha$ for small enough $\alpha > 0$, with

$$\lambda'(0) = \frac{1}{\beta m}.$$

We have now found a critical point $\phi(\lambda)$ of $\mathscr{E}$ which is close to $\phi_m$ for small enough $\alpha > 0$. The critical manifold is obtained by applying the group SU(2) to this critical point.

## § 5. COUPLING TO THE ELECTROMAGNETIC FIELD

If one attempts to apply the scheme of this paper to the coupling of a molecule with the electromagnetic field, one has to cope with possible ultra-violet divergences, infra-red divergences and effects of the $A^2$ term. In his thesis [*19*] Pfeifer proposes a procedure for handling these problems which leads ultimately to the functional $\mathscr{E}$ on $\mathbb{C}^2$ which we discussed in Proposition 9. In a subsequent paper [*20*] he derived by the same procedure the functional $\mathscr{E}$ on $L^2(\mathbb{R}^{3N})$ defined by

$$\mathscr{E}(\phi) = \langle H_0\phi, \phi\rangle + \langle V\phi, \phi\rangle - (2\pi c)^{-2} \int_{\mathbb{R}^3} |\langle g(k)\phi, \phi\rangle \times k|^2 \, |k|^{-4} d^3k \qquad (5.1)$$

which is relevant to a molecule of N distinguishable spinless charged particles. $H_0$ is their kinetic energy operator and V is their potential energy operator due to Coulomb interactions. The vector operator $g(k)$ is defined by

$$g(k) = \frac{1}{2} \sum_{r=1}^{N} \frac{z_r}{m_r} (e^{-ik.Q_r} P_r + P_r e^{-ik.Q_r}).$$

Pfeifer also claims on physical grounds that $\mathscr{E}(\phi)$ must be bounded below, a property which is indeed vital for the physical interpretation. Unfortunately this is incorrect.

THEOREM 19. — If we apply a scale transformation $U_\alpha$ in $L^2(\mathbb{R}^{3N})$ such that

$$U_\alpha^* P_r U_\alpha = \alpha^{-1} P_r$$
$$U_\alpha^* Q_r U_\alpha = \alpha Q_r$$
$$U_\alpha^* g(k) U_\alpha = \alpha^{-1} g(\alpha k)$$
$$U_\alpha^* H_0 U_\alpha = \alpha^{-2} H_0$$
$$U_\alpha^* V U_\alpha = \alpha^{-1} V$$

then

$$\mathscr{E}(U_\alpha \phi) = \alpha^{-2} \langle H_0 \phi, \phi \rangle + \alpha^{-1} \langle V\phi, \phi \rangle - \alpha^{-3}(2\pi c)^{-2} \int_{\mathbb{R}^3} |\langle g(k)\phi, \phi \rangle \times k|^2 \, |k|^{-4} d^3k$$

which converges to $-\infty$ as $\alpha$ converges to zero.

It is clear that this difficulty is caused by the fact that the elimination of the $A^2$ term leads to unphysical ultraviolet divergences as $\alpha \to 0$. According to Pfeifer [*21*] it is possible to redevelop the entire theory of [*20*] while including the $A^2$ term, so as to derive another more complicated non-linear functional $\mathscr{E}'(\phi)$, which is probably bounded below. Moreover the functionals $\mathscr{E}(\phi)$ and $\mathscr{E}'(\phi)$ are approximately equal for $\phi$ of sufficiently small total energy, so a global minimum of $\mathscr{E}'(\phi)$ may be approximately equal to a local minimum of $\mathscr{E}(\phi)$. If this is indeed the case then Theorem 19 is not as distressing as it seems at first sight. As an entirely separate point it would be valuable to investigate the use of the dipole approximation for this problem, already discussed in [*20*], from the point of view of its guage invariance [*29*].

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