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KETS OF BROKEN SYMMETRY IN THE DERIVATION OF MODEL HAMILTONIANS*

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ABSTRACT: Model Hamiltonians are often defined on a space providing a simple zero-order picture of the system under investigation. While the simplest basis kets of this zero-order eigenspace may be of broken symmetry with respect to the full group of the perturbed Hamiltonian, the basis kets often may be transformed into one another by the action of appropriate group elements. In such a case we describe a variational development of the model Hamiltonian. This scheme is based primarily on a single basis ket of broken symmetry; the scheme provides an alternate to the usual perturbative development and is, in principle, exact. Particular reference to the Heisenberg exchange Hamiltonian is made.

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1. INTRODUCTION

In computational work the vector space on which a Hamiltonian is defined may be truncated to a manageable size through the use of physical intuition and experience. Sometimes the calculations are restricted to a space which may be generated from a single "primitive" ket through the action of the elements of a group which commutes with the Hamiltonian. Indeed in simple treatments of Van der Waals interactions, Frenkel excitons, minimal basis Hartree-Fock theory, crystal field theory, atomic shell theory and the theory of interatomic exchange interactions, one often encounters such a restricted "zero-order" space. The typical treatment of these restricted problems invokes the extensively studied methods of symmetry adaptation (see, for instance, references 1, 2 or 3) and then diagonalization in the symmetry subspaces. In extending the treatment beyond this zero-order space one may extend the space and merely symmetry adapt again. Another conventional alternative is to employ degenerate perturbation theory[4] to construct an effective Hamiltonian on the zero-order space and again symmetry adapt and diagonalize.

Here we describe yet another alternative which uses group theory to avoid symmetry adaptation, in the sense that the desired eigenvalues are obtained through a computation of a ket which is of broken symmetry and which resembles the single primitive ket referred to above. Indeed this single primitive ket may be regarded as a zero-order description of the *multistate* ket which we wish to compute.

Although multistate kets have arisen in a vast number of wide-ranging applications as an approximate concept, the realization of a more exact concept in this regard has only infrequently been found in the literature. One early realization of this general concept is found in papers by Koster[5] and Parzen[6] where they propose the use of localized Wannier-type Hartree-Fock orbitals for band theory calculations rather than the common symmetry adapted delocalized Bloch-type Hartree-Fock orbitals. They point out that these localized orbitals are physically appealing and may be obtained by minimizing expectation values of the one-electron Hartree-Fock Hamiltonian subject to symmetry constraints requiring the kets to be of mixed space group symmetry. The group-theoretic aspects arising in this application were further developed by des Cloizeaux[7] and Ruch and Schonhofer[8]. Other schemes not invoking the use of group-theoretic ideas have also been described[9] to directly compute these localized Hartree-Fock orbitals.

Another realization of the general concept of a refined multistate ket occurs in the work of Herring[10] where he proposes a perturbative treatment

for the multistate ket representing a collection of weakly interacting "exchange-coupled" atoms or molecules. In this case the zero-order multistate ket is a simple product of atomic kets and is of mixed permutational symmetry. Several computations using Herring's method have been made[11]. Different perturbation expansions of this multistate ket were suggested by Hirschfelder and Silbey[12], Kirtman[13] and others[14]. These perturbative schemes have been[15] carried out on simple atoms and molecules. Klein[16] suggested a variational scheme for this multistate ket, and applications exhibiting computational advantages have been made[17,18]. Adams[19] has formulated this multistate variational scheme in a different manner. In fact the formulations of Klein and Adams turn out to be formally similar to the group-theoretic[5-8] and non-group-theoretic[9] procedures earlier described for localized Hartree-Fock orbitals.

In the following we shall consider the group-theoretic multistate ket variational scheme indicating some potential computational advantages. An application in deriving the Heisenberg spin Hamiltonian is discussed too.

2. GENERAL THEORY

We consider a Hamiltonian H which commutes with a group $\mathcal{G}$,

$$[H, G] = 0 \quad , \qquad G \in \mathcal{G} \quad . \tag{2.1}$$

We let $|0>$ be a zero-order primitive ket from which we may generate a set of kets

$$\{G|0> \; ; \; G \in \mathcal{G}\} \quad . \tag{2.2}$$

which span a space containing zero-order approximations to the eigenkets of interest. We assume this spanning set (2.2) is linearly independent, although the formalism goes through[16] with only slight modification if it is symmetry adapted to a subgroup of $\mathcal{G}$. If $\mathcal{G}$ is a "complicated" group such as the symmetric group $\mathcal{S}_N$ with N sufficiently large, then diagonalization of H just in the simple zero-order space of (2.2) can pose a difficult problem. If one symmetry adapts with respect to an irreducible representation α of $\mathcal{G}$, the Hamiltonian matrix still has the dimension f^{α} of α. Further evaluation of each individual matrix element on the symmetry adapted basis can be diffi-

cult, if they are to be constructed from first computed primitive matrix elements, as $<0|GH|0>$, $G \in \mathcal{G}$. Extension of the vector space to obtain a more accurate result merely compounds these difficulties.

Some of these problems can hopefully be eased if we vary the *multistate* ket $|\psi>$ to minimize the Hamiltonian expectation value

$$E \equiv <\psi|H|\psi> \tag{2.3}$$

subject to a set of predetermined symmetry constraints

$$<\psi|e^{\alpha}_{rs}|\psi> = a_{ars} \quad . \tag{2.4}$$

Here e^{α}_{rs} is a matric basis element (or Wigner element) of the group algebra of $\mathcal{G}$,

$$e^{\alpha}_{rs} = (f^{\alpha}/g) \sum_{G \in \mathcal{G}} [G^{-1}]^{\alpha}_{sr} G \quad , \tag{2.5}$$

where g is the order of $\mathcal{G}$ and $[G^{-1}]^{\alpha}_{sr}$ is the $(s,r)^{\text{th}}$ element of the α^{th} irreducible representation of $\mathcal{G}$. In addition to the multiplication property

$$e^{\alpha}_{rs} e^{\beta}_{tu} = \delta_{\alpha\beta} \delta_{st} e^{\alpha}_{ru} \quad , \tag{2.6}$$

the matric basis elements also satisfy the relation

$$(e^{\alpha}_{rs})^{\dagger} = e^{\alpha}_{sr} \tag{2.7}$$

if the representation matrices are unitary. The constrained minimization problem is conveniently expressed in terms of Lagrange multipliers $\mathcal{E}_{ars}$ associated with each of the constraints in (2.4),

$$\delta <\psi| H - \sum_{ars} \mathcal{E}_{ars} e^{\alpha}_{rs} |\psi> = 0 \tag{2.8}$$

Letting $[H]^{\nu}$ and $[e^{a}_{rs}]^{\nu}$ be the representations of H and e^{a}_{rs} in the space $\mathcal{U}^{\nu}$ over which $|\psi>$ is varied, we then obtain

$$\left([H]^{\nu} - \sum_{ars} \mathcal{E}_{ars}[e^{a}_{rs}]^{\nu}\right)|\psi> = 0 \quad . \tag{2.9}$$

The term

$$\mathcal{H} \equiv \sum_{ars} \mathcal{E}_{ars}[e^{a}_{rs}]^{\nu} \tag{2.10}$$

which occurs in the multistate ket equation (2.9) may be interpreted as an effective potential or Hamiltonian, which produces the same effect when acting on $|\psi>$ as does $[H]^{\nu}$. We hence expect these Lagrange multipliers $\mathcal{E}_{ars}$ to contain information concerning some of the eigenvalues of H.

To help identify this eigenvalue information, we define the matrix $\mathbf{E}_{a}$ with $(r, s)^{\text{th}}$ element $\mathcal{E}_{ars}$. Then noting that (2.4) and (2.7) imply that $\mathbf{E}_{a}$ is Hermitean, we let $\mathbf{U}_{a}$ be a unitary transformation which diagonalizes $\mathbf{E}_{a}$,

$$\sum_{rs} [\mathbf{U}_{a}]_{\hat{r}r} \mathcal{E}_{ars} [\mathbf{U}^{\dagger}_{a}]_{s\hat{s}} = \delta_{\hat{r}\hat{s}} \mathcal{E}_{a\hat{r}} \quad , \tag{2.11}$$

Further, defining transformed matric basis elements

$$e^{a}_{\hat{r}\hat{s}} \equiv \sum_{rs} [\mathbf{U}_{a}]_{\hat{r}r} e^{a}_{rs} [\mathbf{U}^{\dagger}_{a}]_{s\hat{s}} \tag{2.12}$$

we find that the multistate ket equation (2.9) becomes

$$\left([H]^{\nu} - \sum_{a\hat{r}} \mathcal{E}_{a\hat{r}}[e^{a}_{\hat{r}\hat{r}}]^{\nu}\right)|\psi> = 0 \quad . \tag{2.13}$$

Should the space $\mathcal{U}^{\nu}$, on which the calculation is to be carried out, be invariant to $\mathcal{G}$, then we may apply $[e^{a}_{\hat{r}\hat{r}}]^{\nu}$ to (2.13) and obtain

$$\left([H]^{\nu} - \mathcal{E}_{\alpha\hat{r}} \right) [e^{\alpha}_{\hat{r}\hat{r}}]^{\nu} |\psi> = 0 \quad . \tag{2.14}$$

Hence the $\mathcal{E}_{\alpha\hat{r}}$ are eigenvalues to $[H]^{\nu}$ and the $[e^{\alpha}_{\hat{r}\hat{r}}]^{\nu} |\psi>$ are eigenkets, at least when $\mathcal{U}^{\nu}$ is invariant to $\mathcal{G}$.

In practice we might construct an approximate but accurate multistate ket by variation in a space not invariant to $\mathcal{G}$. In this case we still define the Lagrange multiplier matrix $\mathbf{E}_{\alpha}$ and take its eigenvalues to be approximations to the true eigenvalues. Using a space $\mathcal{U}^{\nu}$ which is not invariant to $\mathcal{G}$ can introduce significant computational savings if it is of significantly smaller dimension than the invariant space induced from $\mathcal{U}^{\nu}$. Also because $\mathcal{U}^{\nu}$ is not necessarily invariant under $\mathcal{G}$; some integrals which would otherwise appear need not. A particular case of interest is when $\mathcal{G}$ is taken as the symmetric group $\mathcal{S}_N$ acting on electronic indices and when the basis of $\mathcal{U}^{\nu}$ is taken to consist primarily of products of atomic kets with given electrons associated with given atoms; in this case multicenter exchange integrals may be avoided. This variational scheme has been successfully carried out[17] for the lowest $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states of the H_2 molecule with $\mathcal{G} = \mathcal{S}_2$ and the avoidance of most of the two-center exchange integrals. These H_2 calculations illustrate the method and some of its possibilities, but the full potential is not realized till larger systems are considered.

3. APPLICATION TO THE DERIVATION OF THE HEISENBERG SPIN HAMILTONIAN

In this section we consider a regular lattice of N equivalent sites each with one unpaired electron for the isolated site limit. A simple Hubbard model is treated which takes into account only one orbital (possibly multiply occupied) on each site, and the limit $N \to \infty$ is ultimately assumed. The group $\mathcal{G}$ is the N-electron symmetric group $\mathcal{S}_N$. Letting φ_i be the orthonormal orbital on the ith site, we see that in order for the multistate ket $|\psi>$ to approach the simple product form

$$|0> \equiv \varphi_1(1) \otimes \varphi_2(2) \otimes \ldots \otimes \varphi_N(N) \tag{3.1}$$

in the isolated site limit, a reasonable choice for $a_{\alpha rs}$ is

$$a_{\alpha rs} = \langle 0 | e^{\alpha}_{rs} | 0 \rangle = \frac{f^{\alpha}}{N!} \delta_{rs} \quad . \tag{3.2}$$

Hence we take this choice.

Rather than working with the matric basis, which we found useful to prove some general characteristics of the scheme, we wish now to employ the group basis of the group algebra. Hence in terms of the group basis the symmetry constraints of (3.2) become

$$\langle \psi | P | \psi \rangle = \sum_{\alpha rs} [P]^{\alpha}_{rs} \langle \psi | e^{\alpha}_{rs} | \psi \rangle = \delta_{P,1} \, , \; P \in \mathfrak{S}_N \tag{3.3}$$

The multistate equation is

$$\delta \langle \psi | H - \mathcal{H} | \psi \rangle = 0 \quad , \tag{3.4}$$

with

$$\mathcal{H} = \sum_{P \in \mathfrak{S}_N} \wp_P P \tag{3.5}$$

corresponding to (2.9) and (2.10).

Next to describe the Hubbard model H and the multistate ket *ansatz* we introduce some notation

$$\begin{aligned} X^{mn}_i &\equiv | \varphi_m(i) \rangle\langle \varphi_n(i) | \equiv m \xleftarrow{i} n \\ X^{mn}_i X^{nm}_i &\equiv m \underset{i}{\overset{j}{\rightleftarrows}} n \end{aligned} \tag{3.6}$$

The commutation properties

$$[X^{mn}_i, X^{pq}_j] = \delta_{ij} (\delta_{np} X^{mq}_i - \delta_{qm} X^{pn}_i) \tag{3.7}$$

of these X-operators show that they span a Lie algebra associated[2] with the N-fold direct product of the unitary group $\mathcal{U}(N)$. Further products of these X-operators may be diagrammatically indicated by ordering the arrows such that lower-lying arrows correspond to operators further to the right in a product. In terms of these X-operators the Hubbard model is

$$H = T \sum_i \sum_{m \sim n} X^{mn} + I \sum_{i<j} \sum_m X_i^{mm} X_j^{mm} \quad , \tag{3.8}$$

where $m \sim n$ indicates sites m and n are nearest neighbors. As is well-known[20] this model embodies the simplest description of a metal ($|T| >> I$), the simplest description of an array of isolated atoms ($|T| << I$), and a variety of interesting situations intermediate between these two extreme limits.

The variational *ansatz* for the unnormalized multistate ket $|\psi>$ is taken to be of the form

$$|\psi> \equiv e^{S^+} |0>$$

$$S^+ \equiv \sum_m S_m^+ + \tfrac{1}{2} \sum_{m \sim n} S_{mn}^+ \quad . \tag{3.9}$$

Here S_m^+ and S_{mn}^+ are 1- and 2-particle excitations from $|0>$,

$$S_m^+ \equiv x \sum_n^{\sim m} X_m^{nm}$$

$$S_{mn}^+ \equiv y X_m^{nm} X_n^{mn} \quad . \tag{3.10}$$

This *ansatz* is similar to that already described elsewhere[21] for antisymmetrized single-state kets. The particle excitation operators all commute with one another, although they do not commute with their adjoints, denoted, for instance, by $S = (S^+)^\dagger$.

Since there are just two variational parameters, x and y, in the *ansatz* of (3.9), we expect not to be able to simultaneoulsy satisfy all the constraints of (3.3). However, for the variational *ansatz* we have taken, we do see that

these constraints will in general be very closely satisfied for permutations $P \in \mathfrak{S}_N$ which transfer electrons among distant sites or which transfer a great number of electrons between near sites. Hence we see that the most important constraints to consider are those for which P is the identity or a nearest neighbor transposition. Further, because of the space group symmetry imposed on our *ansatz*, the constraints for all nearest neighbor transpositions will be satisfied if any one is satisfied. Hence all the nearest neighbor transposition Lagrange multipliers may be taken as equal. Considering only the constraints for these nearest neighbor transpositions, we are then to minimize

$$E = \langle \psi | H - \lambda \sum_{i \sim j} (ij) | \psi \rangle / \langle \psi | \psi \rangle \tag{3.11}$$

subject to the single constraint

$$\langle \psi | (ij) | \psi \rangle = 0 \quad . \tag{3.12}$$

The resulting effective Hamiltonian

$$\mathcal{H} = \lambda \sum_{i \sim j} (ij) \tag{3.13}$$

is seen to be of the form of the conventional nearest neighbor Heisenberg spin Hamiltonian. This present derivation of the Heisenberg spin Hamiltonian differs markedly from the usual general derivations[10, 22-24] which have previously been of a perturbative nature.

The evaluation of the Hamiltonian matrix element is straightforward to obtain the result,

$$E = \sum_{m \sim n} \langle 0 | \{ xT \overset{m}{\underset{n}{\longrightarrow}} + xy\,T \overset{m}{\underset{n}{\rightleftarrows}} + x^2 I \overset{m}{\underset{n}{\circlearrowright}} \} | 0 \rangle A_{(mn)} +$$

$$+ \sum_{\substack{m \sim n \sim p \\ m \neq p}} \langle 0 | \{ x^4 I(1 + 2x^2) \overset{m}{\underset{n}{\circlearrowright}} \overset{p}{\leftarrow} + x^2 y^2 I \overset{m}{\underset{n}{\circlearrowright}} \overset{p}{\circlearrowright} + x^4 y I \overset{m}{\underset{n}{\circlearrowright}} \overset{p}{\rightleftarrows} \} | 0 \rangle A_{(mnp)}$$

$$= N \{ n_{-}(xT + xyT + x^2 I) A_{(12)} + n_{\wedge}(x^4 + 6x^6 + x^2 y^2 + x^4 y) I A_{(123)} \} \tag{3.14}$$

where we have left out the electron-index labels on the arrows, since there is only one allowed choice. The graph-theoretic numbers $n_{\frown}$ and $n_{\wedge}$, which depend only on the lattice[25], are ½ the number of sites bonded to a given site and ⅓ the number of triples of bonded sites involving a given site. The quantities $A_{(m_1 m_2 \ldots m_a)}$ are *residual overlap* matrix elements

$$A_{(m_1 \ldots m_a)} \equiv \frac{<0|\exp(S_{(m_1 \ldots m_a)})\ \exp(S_{(m_1 \ldots m_a)})|0>}{<\psi|\psi>} \qquad (3.15)$$

Recurrence relations for ratios of these residual overlaps are easily obtained,

$$\frac{A_{(m_1 \ldots m_a)}}{A_{(m_1 \ldots m_a n)}} = <0|\{1 + \sum_p{}' x^2 \overleftarrow{n \to p}\}|0> + \sum_p{}' <0|y^2 \circlearrowright_{n\ p}|0> \frac{A_{(m_1 \ldots m_a n p)}}{A_{(m_1 \ldots m_a n)}}$$

$$= 1 + x^2(n_{\frown} - 1) + y^2 \sum_p{}' \left[\frac{A_{(m_1 \ldots m_a n)}}{A_{(m_1 \ldots m_a n p)}}\right]^{-1} \qquad (3.16)$$

where $p \sim n$ and $n_1 p \neq m_1, \ldots, m_a$. Iterating this recurrence relation several times then approximating all the remaining ratios, say by 1, gives an approximation to the desired ratio on the left of (3.16); the more iterations carried out, the more accurate is the result. Convergence appears to be quite rapid for values of $x^2 n_{\frown}$ and $y^2 n_{\frown}$ less than one, as occurs for the values $n_{\frown}|T| \ll I$ of the Hamiltonian parameters.

For the case of a linear chain an analytic solution to these recurrence relations may be obtained[18]. Carrying out numerical computations for such a linear chain, we obtain values for the "exchange" Lagrange multiplier λ. The solution to the Heisenberg model is expected to be simpler[24] than to the full Hubbard model. Since the ground state energy of the linear Heisenberg model is known[26], we obtain a numerical prediction for the ground state energy of the linear Hubbard model. This multistate ket predicted energy is displayed in figure 1, where a perturbation result[23, 24] and the exact[27] Hubbard model ground state energy are also shown. The present simple *ansatz* is seen to improve significantly on the perturbative result, at least for sufficiently large $|T|/I$.

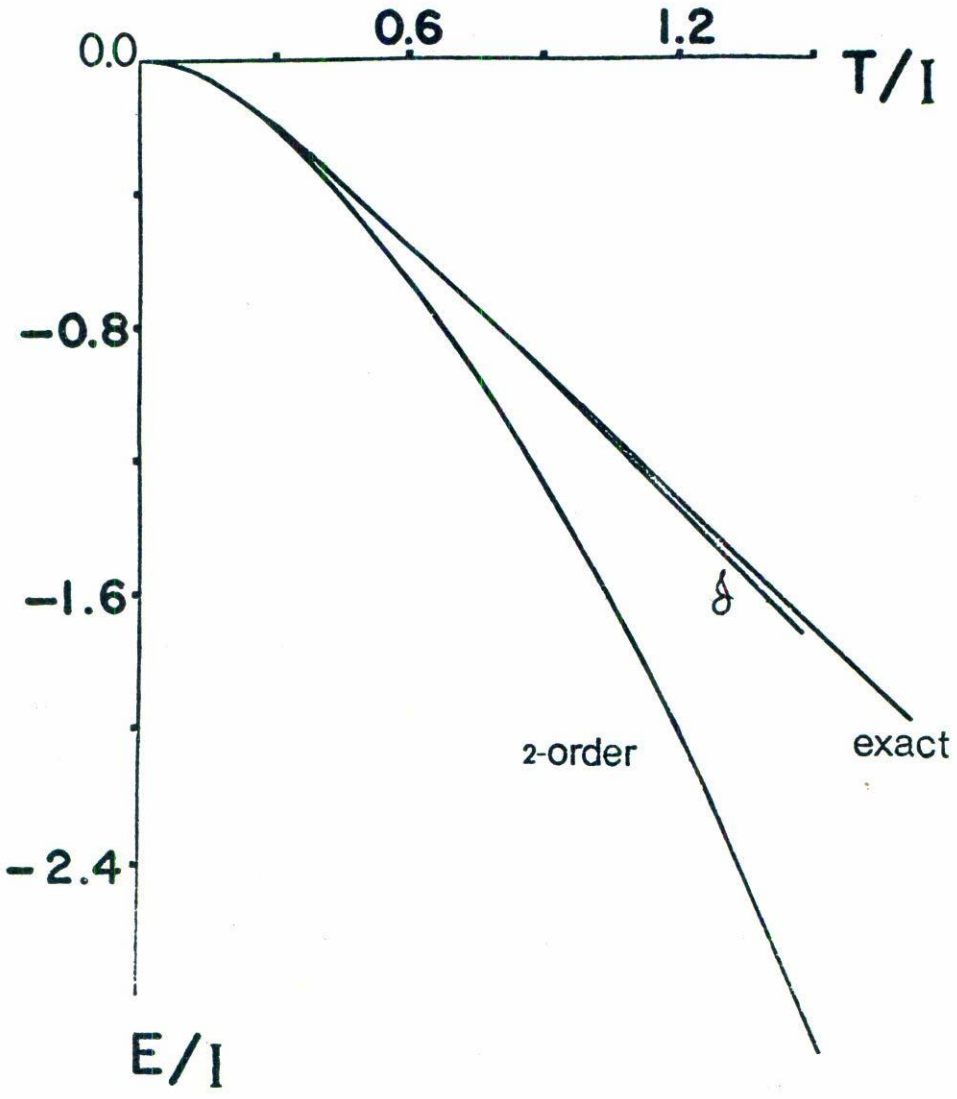

Fig. 1. Comparison of the ground state energies of the linear half-filled Hubbard model as computed by (a) a second-order perturbative method, (b) by the current multistate ket *ansatz*, and (c) an exact treatment.

4. CONCLUSION

It appears that the multistate ket variational scheme has promise as a computational alternative to more conventional schemes. Indeed its characteristics, relating to avoidance of multicenter exchange integrals in molecular calculations and relating to Heisenberg spin Hamiltonian derivations, may be turned to distinct advantage in treatments of suitable problems. Exploration of other characteristics and problems may also be of interest.

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RESUMEN

Los hamiltonianos modelo se definen frecuentemente en un espacio que proporciona una imagen simple, de orden cero, del sistema investigado. Mientras que los kets de la base, más simples de este eigenespacio de orden cero, pueden tener simetría rota con respecto a todo el grupo del hamiltoniano perturbado, los kets de la base pueden frecuentemente transformarse uno en otro, por la acción de los elementos apropiados del grupo. En tal caso describimos un desarrollo variacional del hamiltoniano modelo. Este esquema se basa principalmente en un solo ket básico de simetría rota; el esquema proporciona una alternativa al desarrollo perturbativo usual, y es, en principio, exacto. Se hace particular referencia al hamiltoniano de intercambio de Heisenberg.