

MODEL MOLECULAR HAMILTONIANS

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A generalization of the Wilson–Piech model to molecular systems is introduced. The idea is to exploit an analogy between the problem of critical phenomena and the molecular problem. There are several elements to the method. (a) Hamiltonian formulation on a lattice; (b) the reduction of the number of degrees of freedom of the exact Hamiltonian to a small finite number; (c) focusing on the valence electron properties by coarse graining the lattice degrees of freedom; (d) the qualitative determination of constants associated with kinetic and potential energy from the relation of the model Hamiltonian to the exact Hamiltonian; (e) the determination of the ground state energy of the molecular system by means of a minimum lattice configuration calculation. The model results in a small matrix to be diagonalized, and this matrix is solved by perturbation expansion. The theory is applied to several diatomic molecules. Finally, we explicitly construct a renormalization group transformation that integrates out the core degrees of freedom but retains information about the valence degrees of freedom.

1. Introduction

Molecular electronic structure provides an understanding of physical properties and the reactivities of molecules as well as the reaction pathways of chemical reactions. There are a number of existing methods [1], such as the *ab initio*, the density functional [2] and the pseudopotential [3], for calculating electronic properties in atomic, molecular, and solid state bonding problems. Since the valence electrons largely determine properties such as bond strengths, polarizability, ionization potentials and molecular geometries, attention has recently been focused on new techniques such as the quantum Monte Carlo (QMC) method [4].

QMC is a method of solving the Schrödinger equation stochastically with suitable algorithms. The higher energy associated with the core electrons and sharply varying nuclear potential induce large fluctuations in the energy. This makes accurate calculations of valence electron properties difficult for large atoms and molecules. The point is simply this; the core energy rises as the

square of the nuclear charge Z and the time steps that may be taken in the simulations decrease as Z^{-2} due to reduced phase space of the core electrons. This results in poor sampling of the valence electrons with large variance from the core. This problem has been addressed by a variety of sampling techniques [4] and the use of ab initio effective core potentials as the starting point in QMC calculations. The basis of effective core potentials is to replace the core electrons by an effective potential which contains the core valence repulsion and orthogonality condition. The advantage of treating valence levels only is that the overall $Z^{6.5}$ dependence weakens to $Z_{\text{eff}}^{3.4}$, where Z_{eff} is a screened nuclear charge.

A potentially useful and as yet unexplored method [5] for studying valence electron properties is the renormalization group method [6], conceived by Wilson to handle problems involving a broad range of length and time scales. In this paper we introduce a set of methods for calculating electronic structure of molecular systems based on renormalization group and lattice gauge field theories. The method is a generalization of the Wilson–Piech model [7] and has the same advantage over a continuum calculation as do lattice models of critical phenomena. The behavior of a liquid near its critical point is governed by long wavelength and low energy fluctuations. The basic interactions are short range and are not such low energy. The binding energy of a molecule is attributed to the valence electrons; these electrons have long wavelengths and “low” energies compared to the inner atomic electrons which contribute the bulk of the total energy of a molecule.

In a paper that appeared two decades ago, Wilson and Piech [7] explored the feasibility of the idea mentioned above. These authors developed a lattice model to describe the $n = 1$ and $n = 2$ states of the first and second-row atoms based on several postulates. The model was applied to atoms H to B with the associated isoelectronic sequences. Wilson and Piech found that with a few hours of hand computations the total energies and ionization energies of atoms can be obtained respectively to an accuracy of 2% (or less) and 25% (or less). Although these numbers are of marginal interest from a chemical point of view, the basic ideas were nevertheless impressive. Use of renormalization group techniques and advances in simulation algorithms are needed to extend the Wilson–Piech model.

In this paper a modest attempt is made to extend the Wilson–Piech theory to the case of homonuclear diatoms. There are several ingredients to the methods. (1) We recast the problem as a Hamiltonian formulation on a lattice. (2) The number of degrees of freedom of the exact Hamiltonian is reduced to a small finite number corresponding to a twelve-point lattice. (3) We focus our attention on the valence electron properties by coarse graining the lattice degrees of freedom. The lattice spacing is of the order of the wavelength of the

2s and the 2p electrons and much larger than the wavelength of the 1s electrons. (4) The qualitative determination of the constants associated with the kinetic and potential energy from the relation of the model Hamiltonian to the exact Hamiltonian. (5) The parameters in the Hamiltonian are scaled with respect to the atomic number Z . (6) A diagonal element approximation to the ground state by determining the configuration of minimum energy on the lattice. We introduce the methods in approximately the above order. We have studied a number of molecular systems such as H_2 , H_2^+ , He_2^+ , F_2 , Li_2 , Be_2 , and N_2 and present our results on some of these systems and their excited states.

Finally, we construct a renormalization group transformation (RGT) that integrates out the high energy part associated with the core degrees of freedom. The result is a sequence of effective Hamiltonians that describes the valence electrons. Strategies for solving these equations are briefly discussed.

2. Formulation of the model

The model Hamiltonian for homonuclear diatomic molecules is constructed from the finite difference approximation to the exact molecular, second-quantized Schrödinger Hamiltonian

$$\begin{aligned}
 H = & \frac{1}{2} \sum \int d\mathbf{r} \nabla \psi_\alpha^\dagger(\mathbf{r}) \cdot \nabla \psi_\alpha(\mathbf{r}) - Z \sum_\alpha \int d\mathbf{r} [V_1(\mathbf{r}) + V_2(\mathbf{r})] \psi_\alpha^\dagger(\mathbf{r}) \psi_\alpha(\mathbf{r}) \\
 & + \sum_{\alpha, \beta} \int d\mathbf{r} d\mathbf{r}' V(\mathbf{r} - \mathbf{r}') \psi_\alpha^\dagger(\mathbf{r}) \psi_\beta^\dagger(\mathbf{r}') \psi_\alpha(\mathbf{r}) \psi_\beta(\mathbf{r}'). \quad (1)
 \end{aligned}$$

The $\psi_\alpha^\dagger(\mathbf{r})$, $\psi_\alpha(\mathbf{r})$ are Fermi field operators with spin α , and $V(\mathbf{r})$ is the Coulomb potential. The subscripts on $V(\mathbf{r})$ indicate the nucleus, of atomic number Z , with which the electrons interact. Eq. (1) is in atomic units for which $\hbar = e = m = 1$. All energies and distances are in atomic units (a.u.).

The lattice model consists of treating the molecular Hamiltonian on a spatial lattice and is based on the following postulate:

(i) The electrons are restricted to a twelve-point lattice as shown in fig. 1. The two nuclei are considered fixed at the points o and o' which are at a distance R apart. Each nucleus is surrounded by five sites. The lattice spacing is a .

(ii) The form of the model Hamiltonian is

$$\begin{aligned}
 H = & \sum_{n, \alpha} A_n \psi_{n\alpha}^\dagger \psi_{n\alpha} + \sum_{\substack{n, \alpha \\ m, \beta}} V_{nm} \psi_{n\alpha}^\dagger \psi_{m\beta}^\dagger \psi_{n\alpha} \psi_{m\beta} \\
 & - k \sum_{\alpha, \beta} [(\psi_{x\alpha}^\dagger + \psi_{y\alpha}^\dagger + \psi_{z\alpha}^\dagger + \psi_{-x\alpha}^\dagger + \psi_{-y\alpha}^\dagger) \psi_{\alpha\beta}
 \end{aligned}$$

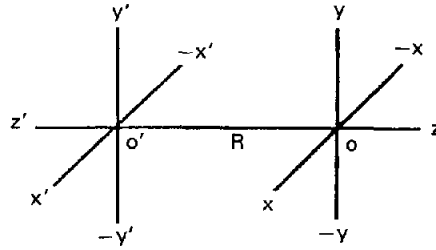


Fig. 1. The twelve point lattice of postulate (i).

$$\begin{aligned}
 & +(\psi_{x'\alpha}^\dagger + \psi_{y'\alpha}^\dagger + \psi_{-x'\alpha}^\dagger + \psi_{-y'\alpha}^\dagger + \psi_{-z'\alpha}^\dagger)\psi_{o'\beta} + \text{adjoints}] \\
 & -\lambda_1 \sum_{\alpha,\beta} (\psi_{o\alpha}^\dagger \psi_{o'\beta} + \text{adjoint}) \\
 & -\lambda_2 \sum_{\alpha,\beta} (\psi_{x\alpha}^\dagger \psi_{x'\beta} + \psi_{y\alpha}^\dagger \psi_{y'\beta} + \psi_{-x\alpha}^\dagger \psi_{x'\beta} + \psi_{-y\alpha}^\dagger \psi_{y'\beta} + \text{adjoints}). \quad (2)
 \end{aligned}$$

The sum over n and m is over the twelve lattice points and ψ_n^\dagger and ψ_n are lattice Fermi creation and annihilation operators obeying anticommutation relations. \mathbf{n} is a three dimensional vector with integral components. To derive eq. (2) we find the discrete version of the continuous operators. The various lattice operators are given by

$$\int d\mathbf{r} \rightarrow a^3 \sum_{\mathbf{n}}, \quad (3a)$$

$$V(\mathbf{r}) \rightarrow V(\mathbf{n}a), \quad (3b)$$

$$\psi(\mathbf{r}) \rightarrow a^{-3/2} \psi(\mathbf{n}a), \quad (3c)$$

$$\nabla \psi(\mathbf{r}) \rightarrow a^{-5/2} \sum_{\boldsymbol{\rho}} [\psi(\mathbf{n}a + \boldsymbol{\rho}a) - \psi(\mathbf{n}a)] \boldsymbol{\rho}, \quad (3d)$$

where $\boldsymbol{\rho}$ are unit vectors in the x , y , z directions. The gradient expansion follows from an application of Taylor's expansion along the Cartesian coordinate axes, and the transformation given by eq. (3c). Eq. (3d) follows by the use of the fermion anticommutation relation

$$\{\psi_n^\dagger, \psi_m\} = \delta_{nm}. \quad (4)$$

We write $\psi(\mathbf{r}) = A\psi_n$, where A is a constant to be determined. Substituting the expression for $\psi(\mathbf{r})$ in eq. (4) gives the value $A = a^{-3/2}$. The kinetic energy term in H thus takes the form

$$\begin{aligned} & \frac{1}{(2a^3)} \sum_n a^{-5} \sum_{\rho, \rho'} [\psi^\dagger(na + \rho a) - \psi^\dagger(na)][\psi(na + \rho' a) - \psi(na)] \rho \cdot \rho' \\ & = \frac{1}{(2a^2)} \sum_n \left\{ 6\psi^\dagger(na) - \sum_\rho \psi^\dagger(na) \psi(na + \rho a) \right\}. \end{aligned} \quad (5)$$

The sum over ρ is over the six unit vectors $\{\pm e_i, i = 1, 2, 3\}$. The potential energy part of the Hamiltonian is transformed to

$$-Za^3 \sum_n V(na) a^{-3} \psi^\dagger(na) \psi(na), \quad (6)$$

while the Coulomb part becomes

$$\sum_n \sum_m V(na - ma) \psi^\dagger(na) \psi^\dagger(ma) \psi(na) \psi(ma). \quad (7)$$

On combining eqs. (3)–(7) we get the model Hamiltonian.

(iii) The parameters A_n , V_{nm} , λ , k appearing in the model Hamiltonian are phenomenological in nature and depend on the internuclear distance R . These will be chosen to fit the experimental spectra in question.

(iv) A_n , k , λ_1 , λ_2 scale as Z^2 from molecule to molecule, V_{nm} as V_{oo} , $R/|R_n - R_m|$, where R_n is the position of the n th site and V_{oo} as Z .

(v) The parameters A_n are chosen to preserve D_{4h} symmetry. Symmetry considerations imply that $A_o = A_{o'}$, $A_x = A_{-x} = A_{-x'} = A_{y'}$, etc.

3. Analysis of the model

Let us examine the plausibility and meaning of these postulates. The purpose of postulate (i) is to make calculations as simple as possible. The introduction of the lattice model reduces the number of degrees of freedom of the exact H to a small finite number. The twelve-point lattice is interpreted as a set of points on which the electrons can sit.

A_n is a measure of the energy of an electron at site n , exclusive of the electron–electron interaction energy V_{nm} . The k terms appear as off-diagonal elements in the Hamiltonian matrix, and allow jumps between a nucleus and the other five points. The effects of the k terms is to mix configurations. λ_1 allows jumps between the two nuclei, while λ_2 allows jumps between the lattice points $\pm x' \rightarrow \pm x$ and $\pm y' \rightarrow \pm y$.

The third postulate is the fundamental philosophy of the lattice model for molecular systems. The error in difference and mesh methods for solving differential equations is directly proportional to the size of the mesh spacing.

The lattice model avoids this problem by regarding the model parameters phenomenologically. The values assigned to these parameters should be of the order of magnitude of the terms in the exact Hamiltonian which they represent. For example, the electron–electron repulsion energy between an electron at site x and an electron at the origin, V_{x0} , scales as a^{-1} . The lattice spacing should be comparable to the extension of molecular electron densities. In order that the central sites be capable of describing 1s atomic orbitals, and the peripheral sites the 2s atomic orbitals, the lattice must describe the region around 6 a.u. well, and thus $a \approx 6$ a.u.

Postulate (iv) indicates how the Hamiltonian parameters should change from molecule to molecule. To get an idea of how various quantities scale, observe that lattice spacing a is proportional to Z^{-1} . k is proportional to a^{-2} and thus scales as Z^{-2} . It can be explicitly shown that $A_o = Z^2\alpha + \beta - Z\gamma$, $A_x = Z^2\delta + \beta - Z^2\gamma R/(a^2 + R^2)^{1/2}$, and $A_z = Z^2\delta - Z\gamma R/(a + R)$, where α , γ , β , δ are functions of R . As $R \rightarrow \infty$, the A 's are seen to scale as Z^2 . We have set $V_{oo} = V_{nn}$ for all sites. This postulate reduces the number of independent parameters and is a necessary condition for the model to have predictive powers.

Finally, postulate (v) identifies certain D_{4h} eigenstates with continuous eigenstates.

4. Results of the model

The problem reduces to the solution of the eigenvalue problem, $H\psi = E\psi$, for eq. (2). In order to get molecular energies one has to construct wavefunctions of the appropriate states with the correct symmetry. The wavefunctions of an N electron system take the form of a set of numbers associated with N lattice points. For example, a one electron eigenstate has the form $\sum_{n,\alpha} c_{n,\alpha} \psi_{n,\alpha}^\dagger |\Omega\rangle$ while a two electron eigenstate takes the form $\sum_{n,\alpha;m,\beta} b_{nm,\alpha,\beta} \psi_{n,\alpha}^\dagger \psi_{m,\beta}^\dagger |\Omega\rangle$. Here $|\Omega\rangle$ is the electron vacuum state and $c_{n,\alpha}$ and $b_{nm,\alpha,\beta}$ are the wave functions consisting of a discrete value for each lattice point or set of lattice points.

The Hamiltonian matrix is reduced by looking at submatrices corresponding to eigenstates of the same irreducible representation of D_{4h} symmetry. The problem reduces to the diagonalization of a finite dimensional matrix. There are no time-consuming integrals to be calculated. A single diagonalization yields the total energy of the molecule. The eigenstates are of a non-product form and exhibit correlation effects.

The independent parameters in the model are V_{oo} , $V_{oo'}$, λ_1 , λ_2 , k , α , β , γ , and δ . In contrast, Wilson and Piech have used seven independent parameters

to describe atomic systems. The parameters are determined to give the best fit on the spectra of the model Hamiltonian to the observed spectra of some molecules. Unique predictions are then made for other molecules.

The total symmetric A_g orbitals for the H_2^+ ion are

$$(o + o')/2^{1/2}, \quad (x + x' + (-x) + (-x') + y + y' + (-y) + (-y'))/8^{1/2}$$

$$\text{and } (z + (-z'))/2^{1/2},$$

with energies $A_o - \lambda_1$, $A_x - \lambda_1$ and Z_z respectively. These are associated respectively with $\sigma_g(1s)$, $\sigma_g(2s)$, and $\sigma_g(2p)$ orbitals of the conventional molecular orbital theory. Note that we have used the notation $2^{-1/2}(\psi_o + \psi_{o'}) \rightarrow 2^{-1/2}(o + o')$. The $\sigma_u(1s)$, $\sigma_u(2s)$ and $\sigma_u(2p)$ orbitals of A_u symmetry are represented by

$$(o - o')/2^{1/2}, \quad (x + (-x) + y + (-y) - x' - (-x') - y' - (-y'))/8^{1/2}$$

$$\text{and } (z - (-z'))/2^{1/2},$$

with energies $A_o + \lambda_1$, $A_x + \lambda_1$, and A_z respectively. Finally, the $\pi_g(2s)$ and $\pi_u(2s)$ orbitals of E_g and E_u symmetry have energies $A_x + \lambda_1$ and $A_x - \lambda_1$; these are represented by doubly degenerate orbitals

$$(x + (-x') - (-x) - (x'))/2, \quad (y + (-y') - (-y) - (y'))/2$$

$$\text{and } (x + x' - (-x) - (-x'))/2, \quad (y + y' - (-y) - (-y'))/2.$$

The matrix elements of the Hamiltonian for the $\sigma_g(1s)$ and $\sigma_u(1s)$ orbitals are used to determine A_o and λ_1 by a fit to calculated [8] energies. The values of the λ parameter, in atomic units, are given in table I.

The lattice wave function for the $X^1\Sigma_g^+$ state of a H_2 molecule must have the form $\{\sigma_1^+\}\{\sigma_2^-\} + \{\sigma_2^+\}\{\sigma_1^-\}$ to preserve spatial and spin symmetries. The subscript labels the electrons while the spin components are denoted by superscripts. This state is constructed from four configurations $(\sigma_g(1s)^+)$ $(\sigma_g(1s)^-)$, $(\sigma_u(1s)^+)$ $(\sigma_u(1s)^-)$, $(\sigma_g(1s)^+)$ $(\sigma_g(2s)^-)$, and $(\sigma_u(1s)^+)$ $(\sigma_u(2s)^-)$. When these configurations are mixed via a variational procedure one ends up with the following energy matrix:

$$\begin{bmatrix} 2A_o + \frac{1}{2}(V_{oo} + V_{oo'}) - 2\lambda_1 & \frac{1}{2}(V_{oo} - V_{oo'}) & -2(2^{1/2})k & 0 \\ \frac{1}{2}(V_{oo} - V_{oo'}) & 2A_o + \frac{1}{2}(V_{oo} + V_{oo'}) + 2\lambda_1 & 0 & -2(2^{1/2})k \\ -2(2^{1/2})k & 0 & A_o + A_x + \frac{1}{2}(V_{xo} + V_{xo'}) - \lambda_1 - \lambda_2 & \frac{1}{2}(V_{xo} - V_{xo'}) \\ 0 & -2(2^{1/2})k & \frac{1}{2}(V_{xo} - V_{xo'}) & A_o + A_x + \frac{1}{2}(V_{xo} + V_{xo'}) \\ & & & + \lambda_1 + \lambda_2 \end{bmatrix} \quad (8)$$

Table I
Values of parameters in the lattice model. The energies and distances are in atomic units.

R	λ_1	λ_2	$V_{oo'}$	V_{oo}	α	β	γ	k	δ
2.0	0.2176	0.0505	0.4510	0.7400	-0.3854	0.4162	0.9159	2.6112	-
3.0	0.1047	0.0392	0.3363	0.6391	-0.4626	0.2629	0.6065	2.8269	-0.1110
4.0	0.0503	0.0299	0.2548	0.5983	-0.5064	0.1855	0.4250	2.4144	-
6.0	0.0107	0.0174	0.1702	0.576	-0.5136	0.1112	0.2656	1.1556	-0.1158

V_{oo} and $V_{oo'}$ are determined from eq. (8) by fitting the ground state energy and the mixing coefficients of the two main contributing configurations $\{gg + uu\}$ with accurate data [9] and are presented in table I. At infinite separation the molecular parameters V_{oo} and A_o attain the separate atoms limits of Wilson and Piech [7]; in contrast $V_{oo'}$ and λ both approach zero. One obtains an estimate of λ_2 from a knowledge of the minima of the $EF^1\Sigma_g^+$ excited state of H_2 .

The reproduced double minimum of the $EF^1\Sigma_g^+$ state of H_2 is shown in fig 2. A comparison of $b^3\Sigma_u^+$ excited state energies of H_2 with accurate calculations [10, 11] is shown in fig. 3. For the $a^3\Sigma_g^+$ state of H_2 we find that the ratio of calculated energy to that given in refs. [10, 11] varies from 1.077 to 1.005 as R varies from 4 a.u. to ∞ . We have used a minimum number of configurations in the evaluation of the energies, namely, $(\sigma_g(1s)^+)(\sigma_u(1s)^+)$ for the $b^3\Sigma_u^+$ state and $(\sigma_g(1s)^+)(\sigma_g(2s)^+)$ and $(\sigma_u(1s)^+)(\sigma_u(2s)^+)$ for the $a^3\Sigma_g^+$ state.

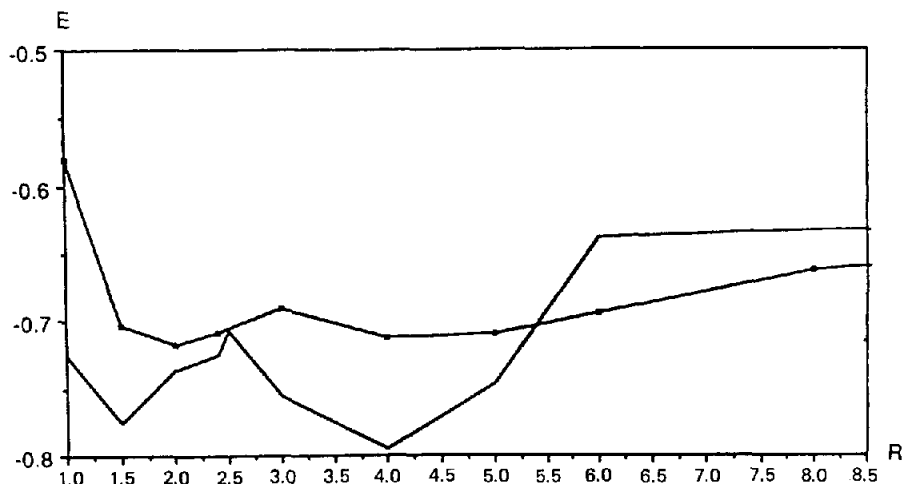


Fig. 2. Comparison of predicted (continuous curve —) total energies of $EF^1\Sigma_g^+$ excited state of H_2 with accurate (continuous dot curve \rightarrow) calculations (ref. [10]). The energies and distances are in atomic units.

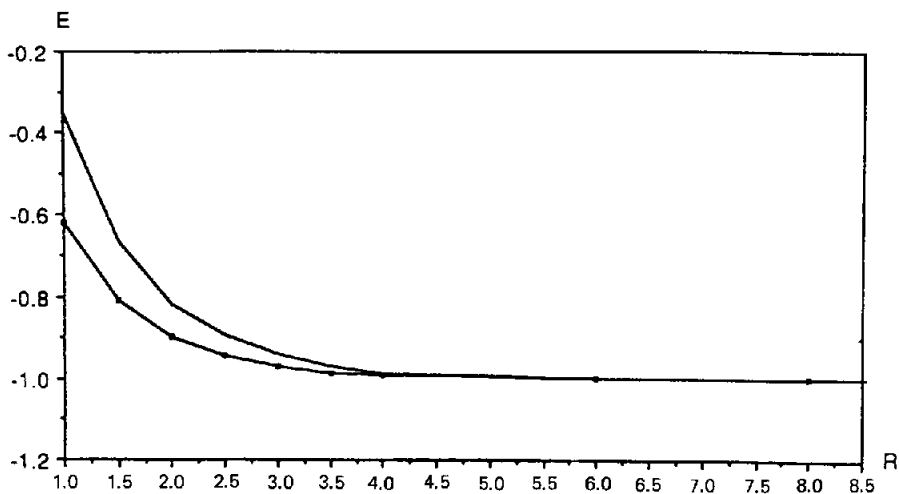


Fig. 3. Comparison of predicted (continuous curve —) total energies of $EF^3\Sigma_u^+$ state of H_2 with accurate (continuous dot curve \rightarrow) calculations (ref. [10]). The energies and distances are in atomic units.

We have also calculated the energy of the first excited $a^3\Sigma_u^+$ state of Li_2 using $(\sigma_g(1s)^+)(\sigma_g(1s)^-)(\sigma_u(1s)^+)(\sigma_u(1s)^-)$ as the core and $(\sigma_g(2s)^+)(\sigma_u(2s)^+)$ as the valence configuration. The ground state of Li_2 is represented by the above core configuration and the following two valence configurations: $(\sigma_g(2s)^+)(\sigma_g(2s)^-)$ and $(\sigma_u(2s)^+)(\sigma_u(2s)^-)$. The matrix elements of the Hamiltonian between these states are minimized, and this leads to a 2×2 energy matrix. The A parameters are adjusted so that the ground state energy is fitted to existing data [12]. At $R = 4.0$ a.u. and $R = 8.0$ a.u. the predicted energies are -14.865 a.u. and -14.877 a.u. respectively. The ratio of calculated to "experimental" energies [13] vary from 0.975 to 0.999 in the range $4 \text{ a.u.} \leq R \leq 8 \text{ a.u.}$ The calculated energies approach the atomic values for large internuclear separation.

The transferability of the parameters between different diatomic molecules is an important test of the theory. We find that the scaling relations of V_{oo} and $V_{oo'}$ from molecule to molecule provide the information necessary to extract the Z dependence of the A parameters. From the A parameters of the diatoms H_2 , $He_2^+(Z=2)$, $Li_2(Z=3)$ and $F_2(Z=9)$, we determine α , β , γ and δ . We test the scaling relations by studying the ground state energies of the $N_2(Z=7)$ molecule. The ground state wavefunction of the N_2 molecule is described by the electron configuration of minimum energy:

$$|y\rangle = \{\sigma^+ \sigma^- \sigma'^+ \sigma'^-\}_{\text{core}} \{x(-x)x'(-x')y(-y)y'(-y')\}_{\text{valence}}.$$

We have dropped the spins from the valence operators for notational simplicity but a linear combination of the operators of appropriate spin and spatial symmetry has been employed. The calculated energies at $R = 2.2$ and $R = 3.0$ are -117.736 a.u. and -118.826 a.u., respectively. The ratio of calculated to “experimental” [13] energies is 1.077 at $R = 2.2$ a.u. and 1.089 at $R = 3.0$ a.u.

Although the energies are not good from a chemical point of view, the results are encouraging enough that it may be fruitful to carry out a rigorous renormalization group transformation of eq. (2). The transformation will project out the “high energy” core electrons but would retain information associated with “low energy” valence electrons. This would yield explicit expressions for the molecular parameters as a function of Z , the lattice spacing and the internuclear spacing. The parameters may then be evaluated, for example, by ab initio methods.

5. Construction of the renormalization group transformation

The basic strategy is to write the lattice Hamiltonian as a sum of two parts,

$$H = H_0 + H_1 . \quad (9)$$

The Hilbert space in which H operates is spanned by the eigenvectors of H_0 . The number of such states is equal to the number of sites N of the lattice. To reduce the degrees of freedom, divide the Hilbert space into two subspaces $\{q\}$ and $\{p\}$, containing N' and $N - N'$ states, respectively. Let $|\psi\rangle$ be an eigenstate of H and denote the projection of $|\psi\rangle$ onto $\{q\}$ by

$$|\psi_q\rangle = Q|\psi\rangle . \quad (10)$$

Then the projected wavefunction satisfies

$$H_q|\psi_q\rangle = E|\psi_q\rangle , \quad (11)$$

where

$$H_q = H_0 + V , \quad (12)$$

and V satisfies the operator equation

$$V = H_1 + H_1[(1 - Q)/(E - H_0)]V . \quad (13)$$

The operator in square brackets in eq. (13) connects only states which are in the excluded space $\{p\}$. We have reduced the problem of diagonalizing an $N \times N$ matrix to that of diagonalizing an $N' \times N'$ matrix provided we can calculate the matrix elements of V in the subspace $\{q\}$. This is non-trivial because one has to solve an operator equation. To overcome this difficulty one can resort to perturbation theory, and expand V in powers of H_1 . Unfortunately, the expression for V is not useful since the effective Hamiltonian is not Hermitian.

However, we can obtain a formula that is Hermitian and involves unperturbed energies in the energy denominator. Define an operator T by the relation

$$(1 - P)|\psi\rangle = TP|\psi\rangle. \quad (14)$$

T denotes the part of $|\psi\rangle$ outside the space projected by P . It is expressed in terms of the part of $|\psi\rangle$ inside the space. T is also assumed to be zero if it acts on states outside the subspace: $T = TP$ and $T = (1 - P)T$.

To find H_{eff} , we write the eigenvalue equation

$$(E - H)(P + T)P|\psi\rangle = 0, \quad (15)$$

in the form

$$E(P + T^\dagger)(P + T)P|\psi\rangle = (P + T^\dagger)H(P + T)P|\psi\rangle. \quad (16)$$

On multiplying this equation by $(1 + TT^\dagger)^{-1/2}$ and making use of the identity $(P + T^\dagger)(P + T) = (1 + T^\dagger T)P$ we get

$$E|\phi\rangle = H_{\text{eff}}|\phi\rangle, \quad (17)$$

where $|\phi\rangle = (1 + TT^\dagger)^{1/2}P|\psi\rangle$ and

$$H_{\text{eff}} = (1 + TT^\dagger)^{-1/2}(P + T^\dagger)H(P + T)(1 + T^\dagger T)^{-1/2}. \quad (18)$$

Note that H_{eff} is Hermitian. To construct T observe that the eigenvalue equation is satisfied, provided

$$(1 - P)HT + (1 - P)H_1P - TPH_1T - TPHP = 0. \quad (19)$$

Since $PH_0P = E_0P$, we can explicitly solve eq. (19) for T :

$$T = (E_0 - H_0)^{-1}(1 - P - T)H_1(P + T). \quad (20)$$

This can be iterated to give T as a power series in H_1 .

A final comment is in order. It can be shown that $(1 + T^\dagger - T)(E - H)|\psi\rangle = 0$. For small H_1 the operator $(1 + T^\dagger - T)$ has an inverse. Thus, $|\psi\rangle$ is an eigenstate of H with eigenvalue E . The eigenstates $|\psi\rangle$ of H are related to the eigenstates of H_{eff} through the formula $|\psi\rangle = (P + T)(1 + T^\dagger T)^{-1/2}|\phi\rangle$. The matrix elements of H_{eff} are zero in the subspace projected by $1 - P$.

It is useful to focus attention on the partition function since any static property involves calculation of $\text{Tr}(O \exp(-\beta H))$, where O is some operator. The renormalization group transformation integrates out high energy scales so as to reduce the cutoff from, say, ε_0 to a new value $\varepsilon < \varepsilon_0$ in such a way that the structure of the energy levels of the Hamiltonian is preserved on the scale of $k_B T$. Energy levels of H with energies much greater than $k_B T$ above the ground state do not contribute. Energy levels which are split on a much finer scale than $k_B T$ get smeared. The transformation replaces the old problem of evaluating $\text{Tr} \exp[-\beta(H_0 + H_1)]$ over states with cutoff ε_0 into a new problem of evaluating $\text{Tr}_p \exp[-\beta(H_0 + H_1(\varepsilon))]$ over states with cutoff $\varepsilon < \varepsilon_0$. The trace Tr_p is taken over the set $\{|p\rangle\}$, which are subsets of eigenstates of H_0 . This is accomplished by perturbation theory as described above. One then repeats the perturbation analysis many times, generating a sequence of Hamiltonians.

The starting point is the following representation of the partition function:

$$Z = \text{Tr} \exp(-\beta H) = \int_C \frac{d\omega}{2\pi i} \exp(-\beta\omega) \sum_\varphi \langle \varphi | (\omega - H)^{-1} | \varphi \rangle. \quad (21)$$

$|\varphi\rangle$ is a complete set of eigenstates of H_0 with energy $\{E_\varphi\}$. The contour C starts from $+\infty$ in a counterclockwise direction, encircles the origin, and then returns to $+\infty$. We use the operator identity

$$(\omega - H_0 - H_1)^{-1} = (\omega - H_0)^{-1} + (\omega - H_0)^{-1} H_1 (\omega - H_0)^{-1} + \dots, \quad (22)$$

to write the n th order term, Z_n , in the perturbation expansion of the partition function as

$$Z_n = \int_C \frac{d\omega}{2\pi i} \exp(-\beta\omega) \sum_{\varphi, \varphi_1, \dots, \varphi_n} \langle \varphi | (\omega - H_0)^{-1} | \varphi_1 \rangle \\ \times \langle \varphi_1 | H_1 (\omega - H_0)^{-1} | \varphi_2 \rangle \dots \langle \varphi_n | H_1 (\omega - H_0)^{-1} | \varphi \rangle, \quad (23)$$

in the form [14]

$$Z_n = -\frac{1}{n} \sum_{\varphi_1, \dots, \varphi_n} \langle \varphi_1 | H_1 | \varphi_2 \rangle \cdots \langle \varphi_n | H_1 | \varphi_1 \rangle \int_{\mathcal{C}} \frac{d\omega}{2\pi i} \exp(-\beta\omega) \times \frac{\partial}{\partial \omega} \left[\prod_{\varphi_i=1}^n (\omega - E_{\varphi_i})^{-1} \right]. \quad (24)$$

An integration by parts lead to the desired result,

$$Z_n = -\frac{\beta}{n} \sum_{\varphi_1, \dots, \varphi_n} \langle \varphi_1 | H_1 | \varphi_2 \rangle \cdots \langle \varphi_n | H_1 | \varphi_1 \rangle \times \left[\sum_{m=1}^n \exp(-\beta E_{\varphi_m}) \prod_{m \neq k} (E_{\varphi_m} - E_{\varphi_k})^{-1} \right]. \quad (25)$$

Note that the quantity within the square parentheses is an analytical function of all energies E_{φ} . The terms up to second order are ($\{|q\rangle\}$ are the remaining eigenstates of H_0)

$$\begin{aligned} Z_0 &\approx \sum_p \exp(-\beta E_p), \\ Z_1 &\approx -\beta \sum_p \langle p | H_1 | p \rangle \exp(-\beta E_p), \\ Z_2 &\approx -\frac{1}{2} \beta \left\{ \sum_{p_1} \sum_{p_2} \langle p_1 | H_1 | p_2 \rangle \langle p_2 | H_1 | p_1 \rangle \right. \\ &\quad \times [\exp(-\beta E_{p_1}) - \exp(-\beta E_{p_2})] / (E_{p_1} - E_{p_2}) \\ &\quad + 2 \sum_q \sum_p \langle p | H_1 | q \rangle \langle q | H_1 | p \rangle \\ &\quad \left. \times [\exp(-\beta E_p) - \exp(-\beta E_q)] / (E_p - E_q) \right\}. \end{aligned} \quad (26)$$

Terms of order $\exp(-\varepsilon/k_B T)$ have been neglected since $\varepsilon/k_B T \gg 1$, and $|p_i\rangle \in \{|p\rangle\}$.

Next consider the question of finding $H_1(\varepsilon)$ such that $\text{Tr}_p \exp\{-\beta[H_0 + H_1(\varepsilon)]\}$ agrees order by order in perturbation theory with the terms in (26). Consider the expansion of $\text{Tr}_p \{\cdots\}$,

$$\text{Tr}_p \exp[-\beta(H_0 + H_1(\varepsilon))] = \text{Tr}_p \exp[-\beta(H_0 + H_1^{(1)}(\varepsilon) + H_1^{(2)}(\varepsilon) + \cdots)]. \quad (27)$$

The right hand side of eq. (27) is also expanded using the perturbation formula eq. (25), and then compared order by order with eq. (26). Comparison of the first-order terms yields the condition

$$-\beta \sum_p \langle p | H_1^{(1)} | p \rangle \exp(-\beta E_p) = Z_1 = -\beta \sum_p \langle p | H_1 | p \rangle \exp(-\beta E_p). \quad (28)$$

This relation is satisfied by the choice

$$H_1^{(1)}(\varepsilon) = PH_1P. \quad (29)$$

P is the projection operator for the entire set $\{|p\rangle\}$. Note that all sums over the states are restricted to the subspace P . However, the conditions on $H_1^{(2)}(\varepsilon)$ and $H_1^{(3)}(\varepsilon)$ are determined by the terms containing at least one set of intermediate states belonging to $Q = 1 - P$,

$$\begin{aligned} & -\beta \sum_p \langle p | H_1^{(2)} | p \rangle e^{-\beta E_p} = \\ & -\beta \sum_q \sum_p \langle p | H_1 | q \rangle \langle q | H_1 | p \rangle [\exp(-\beta E_p) - \exp(-\beta E_q)] / (E_p - E_q), \\ & |q\rangle \in \{|q\rangle\}. \end{aligned} \quad (30)$$

The operator $H_1^{(2)}(\varepsilon)$ satisfies this relation provided it is of the form

$$\begin{aligned} H_1^{(2)}(\varepsilon) = \frac{1}{2} \sum_{\alpha, \beta, q} P_\alpha H_1 |q\rangle \langle q | H_1 P_\beta & (\{1 - \exp[-\beta(E_q - E_\alpha)] / (E_q - E_\alpha)\} \\ & + \{1 - \exp[-\beta(E_q - E_\beta)] / (E_q - E_\beta)\}). \end{aligned} \quad (31)$$

$|\alpha\rangle$ and $|\beta\rangle$ belong to the set $\{|p\rangle\}$ and E_q are the energy eigenvalues of H_0 in states $|q\rangle$. The unintegrated degrees of freedom enter as intermediate states. This is a direct result of the quantum mechanical nature of the system. The expressions also involve energy denominators that vanish; the complete expressions are nonsingular and well behaved.

The recursion relations satisfy the semigroup property and have been derived for a finite cutoff. They can be converted into differential recursion relations by letting $\varepsilon \rightarrow \varepsilon - \delta\varepsilon$. For numerical implementation of these recursion relations it is convenient to generate a sequence of effective Hamiltonians

$$H_{\text{eff}}(m+1) = \mathbb{T}[H_{\text{eff}}(m)],$$

where \mathbb{T} denotes the renormalization group transformation. \mathbb{T} is defined by its input which are the eigenvalues of $H_{\text{eff}}(m)$ and the matrix elements between these eigenstates. As output of \mathbb{T} we get the eigenvalues of $H_{\text{eff}}(m+1)$ and the matrix elements. Numerical implementation of these recursion relations is under way.

6. Discussion

The ground state has been evaluated using the electron configuration of minimum energy on the lattice and calculating the diagonal elements corresponding to this configuration. The diagonal element approximation is based on the fact that corrections to the diagonal elements of the Hamiltonian matrix are small in comparison to the diagonal elements. Here “configuration” refers to the specific location of the electrons on the lattice sites. Each configuration is summed with other equivalent lattice configurations to obtain a wavefunction of proper symmetry. The difficult part of the lattice calculations is the determination of the basis states of the submatrix of given symmetry, and then the calculation of the matrix elements between these states. These calculations get complex for several electron atoms and molecules.

A graphical technique [15] has been developed that makes the calculation simple. A graph depicts the sum of all equivalent graphs having the proper symmetry of the state. We assume that all spin symmetries are accounted for, so that the graphs represent the angular momentum symmetry of the eigenfunctions and any symmetries under spatial interchange of electrons. The graphical procedure makes it easy to count the number of other graphs that add to the proper symmetry, and hence to calculate the normalization factors properly. The matrix elements follow from the normalization factors of the graphs.

The model calculations were surprisingly simple. The molecular energies were obtained qualitatively from the eigenvalues of matrices of low order. Off-diagonal terms in the energy matrix were found to be small.

A disadvantage of the method is that we have not yet found a systematic procedure for the determination of the parameters. For heteronuclear diatomic molecules, and quite generally for polyatomic ones, LCAO-type coefficients would have to be applied rather than the molecular orbitals used here. Further, optimization of the parameters at the N -electron level rather than the one-electron level may lead to complex optimization problems. These points are being investigated.

The model described here does not improve one's ability to compute energy levels which are determined more accurately by other methods. The reason that this model has been described is that there are complicated problems, namely the binding energies of complex molecules, for which existing techniques are not adequate.

The lattice model for molecules has been shown to have advantages over a continuum calculation as do lattice models for critical phenomena. The lattice model for molecules is much easier to solve than a first principal calculation, but nevertheless gives a qualitative understanding of molecular binding. A

synthesis of lattice models and renormalization group techniques developed here may be of potential use in elucidating our understanding of bonding in molecular and solid state problems.

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