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Partition function of the Hueckel model

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Abstract. We obtain the partition function of the Hueckel model through the Feynman path integral formulation. The present formalism appears as a practical tool for the evaluation of thermodynamic and magnetic properties of molecular systems, and constitutes an alternative method to those given previously using the Green's function and Dyson equation to get self-energies and reactivity indices.

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Feynman path integral formulation of quantum mechanics reveals a deep connection between classical statistical mechanics and quantum theory. Indeed in an imaginary time formalism the Feynman integral is mathematically equivalent to a partition function. The purpose of this letter is to get the propagator of the Hueckel model through the path integral formulation. It is shown that the corresponding secular equations can be obtained via the saddle point approximation of the gaussian integrals appearing in the path integral. In particular, we will be concerned with the formalism developed for field theories (which can be illustrated in the context of nonrelativistic quantum mechanics) in order to get more insight in the chemical bonding within the LCAO scheme.

The present formulation constitutes an alternative method to those given previously using the Green's function [1] and Dyson equation [2] to get self energies and reactivities indices.

We apply Feynman formulation of quantum mechanics to a one-dimensional molecular system and consider the amplitude for an electron to propagate between the space-time points (x_a, t_a) and (x_b, t_b). By using a space-time lattice of $N-1$ slices [3,4] and performing the Wick rotation [5] $t = -i\tau$ (t is real time) so as to realize the adequate analytic continuation, one is led to the well-known one-electron euclidean action for discrete time slices [6]. Thus, by expending the eigenket Ψ as a linear combination of atomic orbital $|\phi_i(x_i)\rangle \equiv |x_i\rangle$ an choosing $\tau' - \tau = \varepsilon$ to be infinitesimal so that this interval consists of just one slice, the spectral decomposition

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of the partition function in the site representation can be written as

$$Z_{rs} = \left\langle X_r \left| \exp\left\{-\frac{\varepsilon}{\hbar} H(\Psi, \Psi^*)\right\} \right| x_s \right\rangle, \tag{1}$$

where $H(\Psi, \Psi^*)$, the Hamiltonian in the MO basis set reads ($\langle s, r\rangle$ are site indices)

$$H(\Psi, \Psi^*) = \sum_s |\Psi_s\rangle H_{ss} \langle \Psi_s| + \sum_{\langle r,s\rangle} |\Psi_r\rangle H_{rs} \langle \Psi_s|. \tag{2}$$

The integration measure of the euclidean path integral implies a summation over all path $x(t)$, which start at x_a at time t_a and end at x_b at time t_b. Each path $x(t)$ is weighted by a phase factor determined by the classical action S associated with this path. By using the continuum Ising model, the partition function can be written in the alternative form

$$Z(N) = B \int \prod_{i=1}^{N-1} d\Psi_i d\Psi_{i+1}^* W[\Psi_i, \Psi_{i+1}^*] \exp\left\{\frac{-\varepsilon}{\hbar} H(\Psi_i, \Psi_{i+1}^*)\right\}, \tag{3}$$

where $B = (2\pi h^2 \Delta T)^{-1/2}$, with $\Delta T = t_b - t_a$ and the weight function $W[\Psi_i, \Psi_{i+1}^*]$ is a Dirac δ–function. Eq. (2) constitutes a one-dimensional statistical-mechanical problem. We have a one-dimensional lattice whose sites are labeled with the index i. On each site there is variable x_i which takes on values between $-\infty$ and ∞. The action couples nearest-neighbor variables x_1 and x_{i+1}. Thus, Eq. (2) is identical to the partition function for a one dimensional Ising model. As long as the euclidean version (imaginary time) for the action is begin considered, the δ–function can in fact be represented by its gaussian approximation [7] and $W[\Psi_i, \Psi_{i+1}^*]$ reduces to

$$W[\Psi_i, \Psi_{i+1}^*] = \exp\left\{\frac{-\varepsilon}{\hbar} |\Psi_i\rangle \langle \Psi_{i+1}|\right\} \qquad (\lambda \quad \text{real parameter}). \tag{4}$$

Therefore, an effective Hamiltonian, functional of Ψ, Ψ^*, can be defined in the form

$$H_{\text{eff}}(\Psi, \Psi^*) = H(\Psi, \Psi^*) + \lambda \sum_{r,s} |\Psi_r\rangle \langle \Psi_s|, \tag{5}$$

which clearly represents a constrained Hamiltonian. In fact, the values that a particular MO takes in each of the sites form a finite subset $\{\Psi_r\}$ that fulfills the normalization condition

$$\begin{aligned} 0 < \langle \Psi_r | \Psi_s \rangle < 1 \quad &\text{if } r \neq s, \\ \langle \Psi_r | \Psi_s \rangle = 1 \quad &\text{if } r = s. \end{aligned} \tag{6}$$

On expanding the MO in the atomic orbital basis, Eq. (3) becomes

$$Z(N) = B \int \prod_{i=1}^{N-1} dc_i dc_{i+1}^* \phi_i \phi_{i+1}^* \exp\left\{\frac{-\varepsilon}{\hbar} H_{\text{eff}}(c_i, c_{i+1}^*)\right\}, \tag{7}$$

where c_i are expansion coefficients and $H_{\text{eff}}(c, c^*)$ is given by (S_{ij} are the overlap matrix elements)

$$H_{\text{eff}}(c, c^*) = \sum_i c_i c_i^* H_{ii} + \sum_{\langle i,j \rangle} c_i c_j^* H_{ij} + \lambda \sum_{i,j} c_i c_j^* S_{ij}. \tag{8}$$

The partition function of an M-electron nonrelativistic molecular system, $Q(N)$, can be written as [6]

$$Q(N) = (AB)^N \prod_{\alpha=1}^{M} Z^{(\alpha)}(N), \tag{9}$$

where A is a constant. This is the true partition function and can be calculated if the coefficients c and the overlap (geometry of the molecule) are known. The former can be computed from the saddle point approximations applied to the integral appearing in Eq. (9). Thus, the variation of H_{eff} whit respect to c and c^* leads to the secular equations for confine systems based on the Dirac variational principle [8].

This formalism enables us to study some particular ground-state properties which are obtained or measure only in the presence of an external magnetic field, where it is required that the MO be gauge invariant [9]. Thus, the average magnetization at the site i as well as the magnetic susceptibility can be calculated if the propagator (9) modified in the presence of an external magnetic field is known, which leads to an explicit account of phase transitions and critical phenomena [5]. Therefore, the path integral formalism appears here as a practical tool for the evaluation of thermodynamic and magnetic properties in molecular systems.

Finally, it should be pointed out the Potts model [10] can be used as an alternative method instead of the Ising model for the calculation of the partition function for a molecular system. In such a case one is led to the *ab initio* Hueckel method. In addition, introducing the electronic repulsion operator and expanding each atomic orbital in terms of contracted gaussians, the exchange term can be incorporated in the formalism, thus leading to a bidimensional problem in which the partition function of an *ab initio* SCF method can be evaluated.

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Resumen. Se genera la función de partición del modelo Hueckel a través de la formulación de la integral de línea de Feynman. El presente formalismo aparece como una herramienta práctica para la evaluación de propiedades magnéticas y termodinámicas de sistemas moleculares, y constituye un método alternativo a los reportados previamente usando la función de Green y ecuación de Dyson para obtener auto-energías e índices de reactividad.