

5-2008

The Determination of the Electronic Structure and Geometries of Boron and Boron Mononitrogen Clusters Using an Adaptive, Kink-Based Path Integral Approach to Quantum Mechanics

Shawn Wilkinson

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The Determination of the Electronic Structure and Geometries of Boron and Boron
Mononitrogen Clusters Using an Adaptive, Kink-Based Path Integral Approach to Quantum
Mechanics

by

Shawn Wilkinson

Undergraduate honors thesis under the direction of

Dr. Randall Hall

Department of Chemistry

Submitted to the LSU Honors College in partial fulfillment of
the Upper Division Honors Program.

May, 2008

Louisiana State University
& Agricultural and Mechanical College
Baton Rouge, Louisiana

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Introduction

A recent motivation in studies of condensed phases has been the ability to link microscopic and quantum phenomena with the characteristics of bulk materials. Physical observables such as electrical conductivity, electromagnetic absorption, color, and magnetic phenomena differ between macroscopic bulk materials and their nano-sized equivalents. The ability to predict changes in physical observables through computational and theoretical models has motivated many to develop methods to address the computational challenges that arise from large quantum systems.

One such problem which arises in condensed matter studies involves clusters. A cluster is an aggregate or collection of atomic or molecular species. A cluster can range from a simple system of two atoms to a nano-sized water droplet. In clusters, electron-electron correlation and the inclusion of finite temperature effects on atomic positions are difficult for many quantum mechanic models to address. Due to the many-bodies involved in large clusters, there exist many global and local minima to identify and explore. As cluster size increases, these minima increase drastically, lending a need to develop fast, precise, and accurate computational methods to study these large systems.

A potentially useful method to study clusters is the Feynman path integral formulation of quantum mechanics.¹ In this formulation, electron-electron correlations are taken into consideration as well as the ability to sample different geometries. Another major advantage to the path integral method is the simultaneous treatment of electronic and geometric degrees of freedom. That is, the electronic and geometric optimizations can be calculated independent of one another. Conventional electronic optimization methods require a converged energy or a set of forces to change geometries.

One method to solve the path integral is to use Monte Carlo sampling.² However, the Fermi density matrix poses a difficult problem for Monte Carlo sampling. The problem arises when a matrix product of the electron-electron correlation results in a negative value to be added to the entire summation for the quantum mechanical partition function. The Monte Carlo sampling method does not take into account these negative matrix products, and so large statistical errors can occur. This so-called sign problem has frustrated the path integral approach in determining the partition function for a many-body system.²⁻⁴

One promising method to overcome the sign-problem was developed by Hall.⁵ This method involves recasting the partition function into a basis representation and dividing the paths into small imaginary time intervals. A path will spend some imaginary time in one many-electron state, have a transition to another state, spend some imaginary time in that state, have a transition to another state, etc. Each transition is called a kink, and therefore the entire method is called kink-based path integration (KBPI).

This method has been applied to several different physical and chemical systems.⁵⁻⁷ From previous studies, it has been shown to be very reliable. As an extension to test its reliability, the KBPI method has been applied to boron and boron mono-substituted nitrogen clusters. The electronic and geometric degrees of freedom were studied for each cluster. For each cluster size, an anion and cation form was also studied. From this, the adiabatic detachment energies were determined and the nature of the chemical bonding for boron and boron mono-nitrogen clusters were explored.

Feynman Path Integral

Formalism of the quantum propagator

The time-dependent Schrödinger equation for a non-relativistic particle in a one-dimensional potential $V(x)$ is

$$H\psi(x,t) = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x,t)}{\partial x^2} + V(x)\psi(x,t) = i\hbar \frac{\partial \psi(x,t)}{\partial t} \quad (1.1)$$

which can be rewritten as

$$\left(i\hbar \frac{\partial}{\partial t} - H \right) \psi(x,t) = 0 \quad (1.2)$$

If we define a solution to (1.2) with a function $K(x,t;x_i,t_i)$, where K is the subsequent Green function or propagator of the Schrödinger equation,¹ then (1.2) becomes

$$\left(i\hbar \frac{\partial}{\partial t} - H \right) K(x,t;x_i,t_i) = i\hbar \delta(x - x_i) \delta(t - t_i) \quad (1.3)$$

where δ is the Dirac delta function. For the following initial condition

$$K(x,t_i + 0; x_i, t_i) = \delta(x - x_i) \quad (1.4)$$

It follows then that (1.3) shows that

$$\begin{aligned} \left(i\hbar \frac{\partial}{\partial t} - H \right) \int K(x,t;x_i,t_i) \psi(x_i,t_i) dx_i &= i\hbar \int \delta(x - x_i) \delta(t - t_i) \psi(x_i,t_i) dx_i \\ &= i\hbar \delta(t - t_i) \psi(x,t_i) = 0 \end{aligned} \quad (1.5)$$

Thus,

$$\psi(x,t) = \int K(x,t;x_i,t_i) \psi(x_i,t_i) dx_i \quad (1.6)$$

$K(x,t;x_i,t_i)$ is the probability amplitude for a transition from an initial position x_i and time t_i of the particle to a new position x at later time t .

If the solutions to the stationary wavefunction $\varphi_n(x)$ and the corresponding eigenvalues E_n are known, then an explicit form for the propagator can be found. For a complete system of stationary wavefunctions and $t \geq t_i$, K can be expanded in the basis such that

$$K(x, t; x_i, t_i) = \sum_n a_n \varphi_n(x) e^{-\frac{i}{\hbar} E_n t} \Theta(t - t_i) \quad (1.7)$$

To ensure propagation forward in time, the stepfunction is taken such that $\Theta(t) = 0$ for $t < 0$ and $\Theta(t) = 1$ for $t \geq 0$. From (1.7) it is explicitly taken that the expansion coefficients depend on initial time and position. Because of the initial condition given in (1.4), we have

$$\delta(x - x_i) = \sum_n a_n(x_i, t_i) \varphi_n(x) e^{-\frac{i}{\hbar} E_n t_i} \quad (1.8)$$

Since the left-hand side of (1.8) is time-independent, it follows that

$$a_n(x_i, t_i) = a_n(x_i) e^{+\frac{i}{\hbar} E_n t_i} \quad (1.9)$$

and it follows that

$$\delta(x - x_i) = \sum_n a_n(x_i) \varphi_n(x) \quad (1.10)$$

The closure relation indicates that (1.10) can be fulfilled by

$$a_n(x_i) = \varphi_n^*(x_i) \quad (1.11)$$

Therefore, $K(x, t; x_i, t_i)$ can be represented in terms of the eigenfunctions and eigenvectors of the underlying Hamiltonian

$$K(x, t; x_i, t_i) = \Theta(t - t_i) \sum_n \varphi_n^*(x_i) \varphi_n(x) e^{-\frac{i}{\hbar} E_n (t - t_i)} \quad (1.12)$$

In bra-ket notation, this result can be rewritten as

$$\begin{aligned}
K(x, t; x_i, t_i) &= \sum_n \varphi_n^*(x_i) \varphi_n(x) e^{-\frac{i}{\hbar} E_n (t-t_i)} \\
&= \sum_n \langle n | x_i \rangle e^{-\frac{i}{\hbar} E_n (t-t_i)} \langle x | n \rangle \\
&= \sum_n \langle n | e^{+\frac{i}{\hbar} \hat{H} t_i} | x_i \rangle \langle x | e^{-\frac{i}{\hbar} \hat{H} t} | n \rangle \\
&= \langle x | e^{-\frac{i}{\hbar} \hat{H} (t-t_i)} | x_i \rangle \equiv \langle x | \hat{U}(t, t_i) | x_i \rangle
\end{aligned} \tag{1.13}$$

From (1.13) it follows then that the propagator is simply the time development operator

$$\hat{U}(t, t_i) = e^{-\frac{i}{\hbar} \hat{H} (t-t_i)} \tag{1.14}$$

for $t \geq t_i$ in the x representation. The propagator can also be found written as

$$K(x, t; x_i, t_i) = \langle x | e^{-\frac{i}{\hbar} \hat{H} (t-t_i)} | x_i \rangle \equiv \langle x t | x_i t_i \rangle \tag{1.15}$$

where the time development operator is implied. The notation of (1.15) is that of the Heisenberg representation of quantum mechanics. In this representation the physical state vectors are time-independent and the operators carry the time-dependence, whereas in the Schrödinger representation the wavefunctions carry the time dependence and the operators are time-independent.

Path integral formalism

If the time-interval is sliced into two parts, then the wavefunction is first propagated until the first time interval and then propagated until the end of the second time interval. That is, if t_I is inserted, then

$$\begin{aligned}\psi(x_1, t_1) &= \int K(x_1, t_1; x_i, t_i) \psi(x_i, t_i) dx_i \\ \psi(x, t) &= \int K(x, t; x_1, t_1) \psi(x_1, t_1) dx_1\end{aligned}\tag{1.16}$$

Combining gives

$$\psi(x_1, t_1) = \iint K(x, t; x_1, t_1) K(x_1, t_1; x_i, t_i) \psi(x_i, t_i) dx_i dx_1\tag{1.17}$$

Generalizing to a time interval of $(n + 1)$ equal parts with a specified Δt gives

$$K(x, t; x_i, t_i) = \int \dots \int dx_1 dx_2 \dots dx_n \times [K(x, t; x_n, t_n) K(x_n, t_n; x_{n-1}, t_{n-1}) \dots K(x_1, t_1; x_i, t_i)]\tag{1.18}$$

Equations (1.17) and (1.18) can be viewed as the transition from an initial position and time to a final position and time is the result of the transition from the initial state to all possible intermediate states for each specified time interval until the endpoint is reached. More formally, this can be considered to be integration over all possible paths between the initial state and ending state.¹

For a specified time interval from t_j to t_{j+1} , the propagator can be calculated. From (1.15) and Taylor expanding the exponent, the propagator is

$$\begin{aligned}K(x_{j+1}, t_{j+1}; x_j, t_j) &= \langle x_{j+1} | e^{-\frac{i}{\hbar} \hat{H} \Delta t} | x_j \rangle \\ &\cong \langle x_{j+1} | 1 - \frac{i}{\hbar} \hat{H} \Delta t | x_j \rangle \\ &= \delta(x_{j+1} - x_j) - \frac{i}{\hbar} \Delta t \langle x_{j+1} | \hat{H} | x_j \rangle\end{aligned}\tag{1.19}$$

Using the following definition for the delta function

$$\delta(x - x') = \frac{1}{2\pi} \int e^{-ik(x-x')} dk \quad (1.20)$$

Equation (1.19) becomes

$$K(x_{j+1}, t_{j+1}; x_j, t_j) = \frac{1}{2\pi\hbar} \int e^{\frac{i}{\hbar} p(x_{j+1} - x_j)} dp - \frac{i}{\hbar} \Delta t \langle x_{j+1} | \hat{H} | x_j \rangle \quad (1.21)$$

The Hamiltonian operator is the summation of the kinetic T and potential V operators, and the kinetic and potential operators are functions of the momentum p and position x operators, respectively. If the momentum and position dependencies can be fully separated and all operators are Taylor expandable, then the last term of (1.21) becomes

$$\langle x_{j+1} | \hat{H} | x_j \rangle = \langle x_{j+1} | \hat{T}(\hat{p}) + \hat{V}(\hat{x}) | x_j \rangle \quad (1.22)$$

It then follows for the kinetic part of the summand

$$\begin{aligned} \langle x_{j+1} | \hat{T}(\hat{p}) | x_j \rangle &= \int dp' dp \langle x_{j+1} | p' \rangle \langle p' | \hat{T}(\hat{p}) | p \rangle \langle p | x_j \rangle \\ &= \int dp' dp \langle x_{j+1} | p' \rangle \delta(p' - p) T(p) \langle p | x_j \rangle \\ &= \int dp \langle x_{j+1} | p \rangle T(p) \langle p | x_j \rangle \end{aligned} \quad (1.23)$$

With the normalized momentum eigenfunction

$$\langle x | p \rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{\frac{i}{\hbar} px} \quad (1.24)$$

the following is obtained

$$\langle x_{j+1} | \hat{T}(\hat{p}) | x_j \rangle = \frac{1}{2\pi\hbar} \int e^{\frac{i}{\hbar} p(x_{j+1} - x_j)} T(p) dp \quad (1.25)$$

For the potential part, a similar treatment results in the following

$$\begin{aligned}\langle x_{j+1} | \hat{V}(\hat{x}) | x_j \rangle &= V(x_j) \delta(x_{j+1} - x_j) \\ &= \frac{1}{2\pi\hbar} \int e^{\frac{i}{\hbar} p(x_{j+1} - x_j)} V(x_j) dx\end{aligned}\quad (1.26)$$

Note that on the left-hand side are operators and on the right-hand side are functions. Combining gives

$$\begin{aligned}K(x_{j+1}, t_{j+1}; x_j, t_j) &= \frac{1}{2\pi\hbar} \int e^{-\frac{i}{\hbar} p(x_{j+1} - x_j)} dp \\ &\quad - \frac{i}{\hbar} \Delta t \left(\frac{1}{2\pi\hbar} \int e^{\frac{i}{\hbar} p(x_{j+1} - x_j)} T(p) dp + \frac{1}{2\pi\hbar} \int e^{\frac{i}{\hbar} p(x_{j+1} - x_j)} V(x_j) dx_j \right) \\ &= \frac{1}{2\pi\hbar} \int dp e^{\frac{i}{\hbar} p(x_{j+1} - x_j)} \left(1 - \frac{i}{\hbar} \Delta t H(p, x_j) \right) \\ &\xrightarrow{\Delta t \rightarrow 0} \frac{1}{2\pi\hbar} \int dp_j \exp \left\{ \frac{i}{\hbar} [p_j(x_{j+1} - x_j) - \Delta t H(p_j, x_j)] \right\}\end{aligned}\quad (1.27)$$

Here it is noticed that the propagator between state intervals is no longer associated with the Hamiltonian operator, a relic of quantum mechanical representation of a particle, but the Hamiltonian function, a descriptor from classical mechanics. Thus, the last step indicates that contributions to the propagator can be viewed in terms of the momentum of a classical particle moving from an initial position and time to an ending position and time.

The Hamiltonian path integral is obtained by evaluating (1.18) with (1.27) and taking the limit $n \rightarrow \infty$

$$K(x, t; x_i, t_i) = \lim_{n \rightarrow \infty} \int \prod_{k=1}^n dx_k \int \prod_{k=1}^n \frac{dp_k}{2\pi\hbar} \exp \left\{ \frac{i}{\hbar} \sum_{j=0}^n [p_j(x_{j+1} - x_j) - \Delta t H(p_j, x_j)] \right\} \quad (1.28)$$

where $x_0 = x_i$ and $x_{n+1} = x$. In the limit $n \rightarrow \infty$, the integrand goes from being a complex function of all coordinates and momenta to the whole trajectory. Thus, the exponent becomes

$$\lim_{n \rightarrow \infty} \sum_{j=0}^n \Delta t \left(p_j \frac{(x_{j+1} - x_j)}{\Delta t} - H(p_j, x_j) \right) = \int_{t_i}^t dt' [p(t') \dot{x}(t') - H(p(t'), x(t'))] \quad (1.29)$$

Equation (1.28) can be rewritten in the following abbreviated, symbolic form

$$K(x, t; x_i, t_i) = \int Dx \int Dp \exp \left\{ \frac{i}{\hbar} \int_{t_i}^t dt' [p(t') \dot{x}(t') - H(p(t'), x(t'))] \right\} \quad (1.30)$$

where Dx and Dp stand for the products of differential lengths and differential momenta, respectively.

Equation (1.30) is the path integral formalism of quantum mechanics. It allows the calculation of the propagator, and thus the solution to the Schrödinger equation, in terms of a path integral over classical trajectories.

Connecting classical trajectories with the quantum propagator

At this point, it has not been indicated that the momentum is the canonical conjugate to the coordinate. Therefore, though the exponential integrand looks like the classical action, it cannot be expressed as such in the general case of the path integral. However, if the Hamiltonian depends on the momentum quadratically, it can be shown that the path integration over the momentum can be performed and the action appears.

Let the Hamiltonian be the following special case

$$H = \frac{p^2}{2m} + V(x) \quad (1.31)$$

Equation (1.28) can be expressed as

$$K(x, t; x_i, t_i) = \lim_{n \rightarrow \infty} \int \prod_{k=1}^n dx_k \int \prod_{k=1}^n \frac{dp_k}{2\pi\hbar} \exp \left\{ \frac{i}{\hbar} \Delta t \sum_{j=0}^n \left[p_j \frac{(x_{j+1} - x_j)}{\Delta t} - \frac{p_j^2}{2m} - V(x_j) \right] \right\} \quad (1.32)$$

Using the following integral relation for Gaussian integrals

$$\int_{-\infty}^{+\infty} e^{-ap^2+bp+c} dp = \sqrt{\frac{\pi}{a}} e^{\frac{b^2}{4a}+c} \quad (1.33)$$

the p -integration can be performed with the following results

$$K(x, t; x_i, t_i) = \lim_{n \rightarrow \infty} \left(\frac{m}{2\pi\hbar i \Delta t} \right)^{\frac{n+1}{2}} \int \prod_{k=1}^n dx_k \exp \left\{ \frac{i}{\hbar} \Delta t \sum_{j=0}^n \left[\frac{m}{2} \left(\frac{x_{j+1} - x_j}{\Delta t} \right)^2 - V(x_j) \right] \right\} \quad (1.34)$$

Performing the limit gives

$$K(x, t; x_i, t_i) = \int Dx \exp \left\{ \frac{i}{\hbar} \int_{t_i}^t dt' \left[\frac{m}{2} \dot{x}(t')^2 - V(x) \right] \right\} \times \lim_{n \rightarrow \infty} \left(\frac{m}{2\pi\hbar i \Delta t} \right)^{\frac{n+1}{2}} \quad (1.35)$$

The Lagrangian is defined as

$$L(x, \dot{x}) = \frac{m}{2} \dot{x}^2 - V(x) \quad (1.36)$$

and the action is defined as

$$S[x(t)] = \int_{t_i}^t L(x(t'), \dot{x}(t')) dt' \quad (1.37)$$

Therefore, (1.35) can be rewritten in terms of the action

$$K(x, t; x_i, t_i) = N \int Dx e^{\frac{i}{\hbar} \int_{t_i}^t L(x(t'), \dot{x}(t')) dt'} = N \int Dx e^{\frac{i}{\hbar} S[x(t)]} \quad (1.38)$$

where for this case

$$N = \lim_{n \rightarrow \infty} \left(\frac{m}{2\pi\hbar i \Delta t} \right)^{\frac{n+1}{2}} \quad (1.39)$$

A problem arises in (1.39) when the limit is taken. The value is complex and becomes infinite

when the limit is evaluated and the time interval is made infinitesimal. This problem is

bypassed, however, in physical systems since physical systems require a normalized propagator.¹

Thus the propagator K has been reduced to a path integral by using a Hamiltonian which is quadratic in p . Equation (1.38) indicates that the probability amplitude for going from an initial state to a final state is given by the Lagrangian phase summed over all possible trajectories from the initial state to the final state.

It should be noted that the previous formalisms were all undertaken with the consideration of a one-dimensional particle. The extension to N dimensions is not a difficult task and obtains similar results so long as the dependencies expressed previously are maintained.

Connecting statistical mechanics with quantum mechanics

To go from (1.32) to (1.34), an integration on an oscillatory integrand over an infinite interval was performed. The mathematical trick used was the Gaussian relation (1.33). However, to apply the relation the imaginary time interval $i\Delta t$ was treated as if it were real. More formally, (1.32) was analytically continued into the complex plane by setting the time interval $\Delta t \rightarrow i\Delta t'$ where $\Delta t'$ is either positive or negative. Thus, time was set $t \rightarrow it$, and velocities set $\dot{x} \rightarrow -i\dot{x}$. This is a Wick's rotation which allows the action to be expressed in terms of Euclidean space.

$$S_E = \int_{t_i}^t \left(\frac{m}{2} \dot{x}^2 + V(x) \right) dt \quad (1.40)$$

The propagator becomes

$$K_E(x, t; x_i, t_i) = N \int_{t_i}^t Dx e^{\frac{1}{\hbar} S_E} \quad (1.41)$$

Equation (1.41) looks very much like the partition function in statistical mechanics. The partition function Q from classical mechanics is

$$Q_{cl}(T) \equiv \int \prod_n \frac{dp_n dq_n}{2\pi\hbar} e^{-H(p_n, q_n)/k_B T} \quad (1.42)$$

where p is the momentum, q is the general coordinate, k_B is the Boltzmann constant, and T is the temperature. The quantum statistical partition function is similar to (1.42). Instead of being an integral over phase space, the quantum statistical partition function is the trace of the Hilbert space, or the sum of the diagonal matrix elements

$$Q_{qs}(T) \equiv \text{Tr}(e^{-\hat{H}/k_B T}) = \text{Tr}(e^{-\hat{H}(\hat{p}, \hat{x})/k_B T}) = \sum_j \langle x_j | e^{-\hat{H}(\hat{p}, \hat{x})/k_B T} | x_j \rangle \quad (1.43)$$

Note that the x -operator is used instead of the general coordinate so that the system is quantized canonically.

The propagator, (1.15), and the quantum statistical partition function look very similar. Define the trace of the time development operator as the quantum mechanical partition function.

$$Q_{qm} = \text{Tr}(\hat{U}(t, t_i)) = \text{Tr}\left(e^{-\frac{i}{\hbar}\hat{H}(t-t_i)}\right) \quad (1.44)$$

If the time interval of the quantum mechanical partition function is continued to the negative imaginary value, then the quantum statistical partition function emerges

$$t - t_i = -\frac{i\hbar}{k_B T} \equiv -i\hbar\beta \quad (1.45)$$

where β is the Boltzmann factor. This result directly links the path integral formalism with statistical mechanics.

Kink-Based Path Integral

The previous formalism of the Feynman path integral utilized a position representation. However, one of the inherent problems of using the position representation is the necessity to solve a quantum problem involving atomic positions with electron-electron correlations.⁵⁻⁷ In order to avoid said problem, finite basis sets will be utilized. Finite basis sets have been shown to produce accurate results for many systems.⁸ Reproduced is the complete formalism of the KPBI method.⁵

Formalism with fixed atomic positions

Assume a set of finite, orthonormal, N -particle states. In terms of these states $\{\alpha_j\}$, the partition function can be written

$$Q = \text{Tr}(e^{-\beta\hat{H}}) = \sum_j \langle \alpha_j | e^{-\beta\hat{H}} | \alpha_j \rangle \quad (2.1)$$

This can be discretized using the Trotter theorem

$$\begin{aligned} Q &= \lim_{P \rightarrow \infty} Q(P) \\ Q(P) &= \sum_{j_1, j_2, j_3, \dots, j_P} \langle \alpha_{j_1} | \exp\left(-\frac{\beta}{P} H\right) | \alpha_{j_2} \rangle \times \langle \alpha_{j_2} | \exp\left(-\frac{\beta}{P} H\right) | \alpha_{j_3} \rangle \times \dots \\ &\quad \times \langle \alpha_{j_P} | \exp\left(-\frac{\beta}{P} H\right) | \alpha_{j_1} \rangle \end{aligned} \quad (2.2)$$

The introduction of P allows temperature approximations for the matrix elements. The sign problem can be easily seen in (2.2). Each matrix element can be either positive, negative, or zero. This means that some summands may be negative. Thus, during a Monte Carlo simulation, the sign of the estimator for Q can alternate signs, which leads to large statistical errors. To overcome the sign problem, expand (2.2) by recasting the sum over the matrix

products as a sum with all matrix products of equivalent bases, a matrix product with one basis different from another, etc.

$$\begin{aligned}
Q(P) = & \sum_{j_1,} \left[\left\langle \alpha_{j_1} \left| \exp\left(-\frac{\beta}{P} H\right) \right| \alpha_{j_1} \right\rangle \right]^P \\
& + \sum_{j_1, j_2} \sum_{n=0}^{P-2} \left[\left\langle \alpha_{j_1} \left| \exp\left(-\frac{\beta}{P} H\right) \right| \alpha_{j_2} \right\rangle \right]^n \times \left[\left\langle \alpha_{j_2} \left| \exp\left(-\frac{\beta}{P} H\right) \right| \alpha_{j_3} \right\rangle \right]^{P-2-n} \\
& \times \left[\left\langle \alpha_{j_P} \left| \exp\left(-\frac{\beta}{P} H\right) \right| \alpha_{j_1} \right\rangle \right]^2 + \dots
\end{aligned} \tag{2.3}$$

This is a kink expansion where the first term is the zero kink term and the second is the two kink term, etc.^{9,10} Let

$$\varepsilon = \beta / P \tag{2.4}$$

$$x_j = \left\langle \alpha_j \left| \exp(-\varepsilon H) \right| \alpha_j \right\rangle \tag{2.5}$$

$$t_{ij} = \left\langle \alpha_i \left| \exp(-\varepsilon H) \right| \alpha_j \right\rangle \tag{2.6}$$

Then (2.3) can be rewritten as

$$Q(P) = \sum_j x_j^P + \sum_{n=2}^P \left(\prod_{i=1}^n \sum_{j_i} \right) \left(\prod_{k=1}^n t_{j_k, j_{k+1}} \right) \times \left(\prod_{k=1}^n \sum_{l_k=0}^{P-n} \right) \left(\prod_{k=1}^n x_{j_k}^{l_k} \right) \delta_{l_1+l_2+\dots+l_n, P-n} \tag{2.7}$$

where the first term is the zero kink term and $j_{P+1} \equiv j_1$. Since there are $\binom{P}{n}$ ways to organize n

kinks at P sites, the location of the first kink can be chosen. This rewrites (2.7) as

$$\begin{aligned}
Q(P) = & \sum_j x_j^P + \sum_{n=2}^P \frac{P}{n} \left(\prod_{i=1}^n \sum_{j_i} \right) \left(\prod_{k=1}^n t_{j_k, j_{k+1}} \right) \\
& \times \sum_{l_n=0}^{P-n} \sum_{l_{n-1}=0}^{P-n-l_n} \dots \sum_{l_2=0}^{P-n-l_n-l_{n-1}-\dots-l_3} x_{j_n}^{l_n} x_{j_{n-1}}^{l_{n-1}} \dots x_{j_2}^{l_2} x_{j_1}^{P-n-l_n-l_{n-1}-\dots-l_2}
\end{aligned} \tag{2.8}$$

Let

$$S_j \equiv l_n + l_{n-1} + \dots l_j \tag{2.9}$$

Then (2.8) is

$$Q(P) = \sum_j x_j^P + \sum_{n=2}^P \frac{P}{n} \left(\prod_{i=1}^n \sum_{j_i} \right) \left(\prod_{k=1}^n t_{j_k, j_{k+1}} \right) \times \sum_{l_n=0}^{P-n} \sum_{l_{n-1}=0}^{P-n-S_n} \dots \sum_{l_2=0}^{P-n-S_3} x_{j_n}^{l_n} x_{j_{n-1}}^{l_{n-1}} \dots x_{j_2}^{l_2} x_{j_1}^{P-n-S_2} \quad (2.10)$$

Consider the summand of the second summation. Assume that $x_{j_1} \neq x_{j_2} \neq \dots x_{j_n}$ and let

$$S(\{x_j\}, n) = \sum_{l_n=0}^{P-n} \dots \sum_{l_2=0}^{P-n-S_3} x_{j_n}^{l_n} x_{j_{n-1}}^{l_{n-1}} \dots x_{j_2}^{l_2} x_{j_1}^{P-n-S_2} \quad (2.11)$$

Using the identity

$$\sum_{i=0}^M \binom{x_i}{x_1}^l = \frac{1 - \left(\frac{x_i}{x_1} \right)^{M+1}}{1 - \left(\frac{x_i}{x_1} \right)} \quad (2.12)$$

It is determined that

$$\begin{aligned} \sum_{l_2=0}^{P-n-S_3} x_{j_2}^{l_2} x_{j_1}^{P-n-S_2} &= \sum_{l_2=0}^{P-n-S_3} \left(\frac{x_{j_2}}{x_{j_1}} \right)^{l_2} x_{j_1}^{P-n-S_3} \\ &= x_{j_1}^{P-n-S_3} \left(\frac{1 - \left(\frac{x_{j_2}}{x_{j_1}} \right)^{P-n-S_3+1}}{1 - \frac{x_{j_2}}{x_{j_1}}} \right) \\ &= \frac{x_{j_1}^{P-n-S_3+1} - x_{j_2}^{P-n-S_3+1}}{x_{j_1} - x_{j_2}} \\ &= \sum_{k=1}^2 \frac{x_{j_k}^{P-n-S_3+1}}{\prod_{m \neq k}^2 (x_{j_k} - x_{j_m})} \equiv S(\{x_j\}, 2, n) \end{aligned} \quad (2.13)$$

A general form of $S(\{x_j\}, n)$ can be developed. Assume that

$$S(\{x_j\}, i-1, n) = \sum_{k=1}^{i-1} \frac{x_{j_k}^{P-n-S_i+1}}{\prod_{m \neq k}^{i-1} (x_{j_k} - x_{j_m})} \quad (2.14)$$

The next summation in (2.11) is

$$\begin{aligned}
S(\{x_j\}, i, n) &= \sum_{l_i=0}^{P-n-S_{3+1}} x_{j_i}^{l_i} \sum_{k=1}^{i-1} \frac{x_{j_k}^{P-n-S_i+(i-2)}}{\prod_{m \neq k}^{i-1} (x_{j_k} - x_{j_m})} \\
&= \sum_{l_i=0}^{P-n-S_{3+1}} x_{j_i}^{l_i} S(\{x_j\}, i-1, n) \\
&= \sum_{l_i=0}^{P-n-S_{3+1}} x_{j_i}^{l_i} \sum_{k=1}^{i-1} \frac{x_{j_k}^{P-n-S_i-l_i+(i-2)}}{\prod_{m \neq k}^{i-1} (x_{j_k} - x_{j_m})} \\
&= \sum_{k=1}^{i-1} \frac{x_{j_k}^{P-n-S_i+(i-2)}}{\prod_{m \neq k}^{i-1} (x_{j_k} - x_{j_m})} \left(\frac{1 - \left(\frac{x_{j_i}}{x_{j_k}} \right)^{P-n-S_{3+1}+1}}{1 - \left(\frac{x_{j_i}}{x_{j_k}} \right)} \right) \\
&= \sum_{k=1}^{i-1} \frac{x_{j_k}^{P-n-S_i+(i-1)}}{\prod_{m \neq k}^{i-1} (x_{j_k} - x_{j_m})} - \sum_{k=1}^{i-1} \frac{x_{j_k}^{i-2} x_{j_k}^{P-n-S_i+(i-2)}}{(x_{j_k} - x_{j_i}) \prod_{m \neq k}^{i-1} (x_{j_k} - x_{j_m})}
\end{aligned} \tag{2.15}$$

Now

$$\begin{aligned}
-\sum_{k=1}^{i-1} \frac{x_{j_k}^{i-2} x_{j_k}^{P-n-S_i-l_i+(i-2)}}{(x_{j_k} - x_{j_i}) \prod_{m \neq k}^{i-1} (x_{j_k} - x_{j_m})} &= \frac{x_{j_k}^{P-n-S_{i+1}+1}}{\prod_{m \neq i}^i (x_{j_i} - x_{j_m})} \times \sum_{k=1}^{i-1} \frac{\left(\frac{x_{j_k}}{x_{j_i}} \right)^{i-2} \prod_{m \neq i}^i (x_{j_i} - x_{j_m})}{(x_{j_k} - x_{j_i}) \prod_{m \neq k}^{i-1} (x_{j_k} - x_{j_m})} \\
&= \frac{x_{j_k}^{P-n-S_{i+1}+(i-1)}}{\prod_{m \neq i}^i (x_{j_i} - x_{j_k})} \sum_{k=1}^{i-1} \frac{\left(\frac{x_{j_k}}{x_{j_i}} \right)^{i-2} \prod_{m \neq i}^{i-1} (x_{j_i} - x_{j_m})}{(x_{j_k} - x_{j_i}) \prod_{m \neq k}^{i-1} (x_{j_k} - x_{j_m})} \\
&= \frac{x_{j_k}^{P-n-S_{i+1}+(i-1)}}{\prod_{m \neq i}^i (x_{j_i} - x_{j_k})} \frac{1}{x_{j_i}^{i-2}} \sum_{k=1}^{i-1} \frac{\prod_{m \neq i}^{i-1} (x_{j_i} - x_{j_m})}{\prod_{m \neq k}^{i-1} \left(1 - \frac{x_{j_m}}{x_{j_k}} \right)}
\end{aligned} \tag{2.16}$$

Now

$$\sum_{k=1}^{i-1} \frac{\prod_{m \neq i}^{i-1} (x_{j_i} - x_{j_m})}{\prod_{m \neq k}^{i-1} \left(1 - \frac{x_{j_m}}{x_{j_k}} \right)} = \sum_{k=1}^{i-1} l_k(x_{j_i}) \tag{2.17}$$

This is an $i-2$ order polynomial in x_{j_i} . Consider the function $y(x) = \sum_{k=1}^{i-1} l_k(x)$, which is an $i-2$ order polynomial in x . Since $l_k(x_{j_i}) = x_{j_i}^{i-2} \delta_{k,i}$, $y(x)$ is an $i-2$ order polynomial that has the value $x_{j_k}^{i-2}$ at the $i-1$ points $x_{j_1}, x_{j_2}, \dots, x_{j_n}$. Since $y(x)$ is an $i-2$ order polynomial, it follows that

$$\sum_{k=1}^{i-1} l_k(x) = x_{j_i}^{i-2}. \text{ Therefore,}$$

$$\frac{1}{x_{j_i}^{i-2}} \sum_{k=1}^{i-1} \frac{\prod_{m \neq i}^{i-1} (x_{j_i} - x_{j_m})}{\prod_{m \neq k}^{i-1} \left(1 - \frac{x_{j_m}}{x_{j_k}}\right)} = 1 \quad (2.18)$$

Evaluating (2.15) with (2.17) and (2.18) gives

$$S(\{x_j\}, i, n) = \sum_{k=1}^i \frac{x_{j_k}^{P-n-S_{i+1}+(i-1)}}{\prod_{m \neq k}^i (x_{j_k} - x_{j_m})} \quad (2.19)$$

Thus, by induction, it is shown that

$$S(\{x_j\}, n) = \sum_{k=1}^i \frac{x_{j_k}^{P-1}}{\prod_{k \neq m}^n (x_{j_k} - x_{j_m})} \quad (2.20)$$

Consider the case when some x_{j_k} are equal. Let x_0 occur twice in the following sum

$$\dots \sum_{k=0}^{P-m} x_0^k \sum_{l_1=0}^{P-m-k} x_1^{l_1} \sum_{l_2=1}^{P-m-k-S_1} x_2^{l_2} \dots \sum_{l_n=0}^{P-m-k-S_{n-1}} x_n^{l_n} \times \sum_{j=0}^{P-m-k-S_n} x_0^j \sum_{i=0}^{P-m-k-S_n-j} x_i^i \dots \quad (2.21)$$

The identity

$$\dots \sum_{k=0}^M x_0^k \sum_{l_1=0}^{M-k} x_1^{l_1} = \sum_{k=0}^M x_0^k \sum_{l_1=0}^{M-k} x_1^l \quad (2.22)$$

Thus (2.21) becomes

$$\dots \sum_{k=0}^{P-m} x_0^k \sum_{l_1=0}^{P-m-k} x_0^j \sum_{l_2=1}^{P-m-k-j} x_1^{l_1} \dots \quad (2.23)$$

If there are s identical x_0 , it can be shown that

$$\begin{aligned} & \dots \sum_{k_1=0}^{P-m} \sum_{k_2=0}^{P-m-S_1} \sum_{k_3=0}^{P-m-S_2} \dots \sum_{k_s=0}^{P-m-S_{k_s}} x_0^{k_1+k_2+k_3+\dots+k_s} \times \sum_{l=0}^{P-m-S_{k_s}} x_l^l \dots \\ &= \dots \sum_{k_1=0}^{P-m} \sum_{k_2=0}^{P-m-S_1} \sum_{k_3=0}^{P-m-S_2} \dots \sum_{k_{s-1}=0}^{P-m-S_{k_{s-1}-2}} \sum_{k_s=0}^{P-m-S_{k_s}} x_0^{k_s} \times \sum_{l=0}^{P-m-k_2} x_l^l \dots \\ &= \dots \sum_{k_s=0}^{P-m} x_0^{k_s} \sum_{k_1=0}^{k_s} \sum_{k_2=0}^{k_s-S_1} \dots \sum_{k_{s-1}=0}^{k_s-S_{k_{s-1}-2}} \sum_{l=0}^{P-m-S_{k_s}} x_l^l \dots \end{aligned} \quad (2.24)$$

Where the identity $\sum_{k=0}^{M-N} \sum_{j=k+N}^M = \sum_{j=N}^M \sum_{k=0}^{j-N}$ was used. Define a new identity

$$W(s, k_s) \equiv \sum_{k_1=0}^{k_s} \sum_{k_2=0}^{k_s-S_1} \dots \sum_{k_{s-1}=0}^{k_s-S_{k_{s-1}-2}} \quad (2.25)$$

It is asserted that $W(s, k_s) = \binom{k_s+s-1}{s-1}$. If $W(s-1, k_s - k_1) = \binom{k_s-k_1+s-2}{s-2}$, then

$$\begin{aligned} W(s, k_s) &= \sum_{k_1=0}^{k_s} \binom{k_s-k_1+s-2}{s-2} = \sum_{k_1=0}^{k_s} \frac{(k_s - k_1 + s - 2)!}{(s-2)!(k_s - k_1)!} \\ &= \sum_{k_1=-k_s}^0 \frac{(k_1 + s - 2)!}{(s-2)!(-k_1)!} = \sum_{k_1=0}^{k_s} \frac{(k_1 + s - 2)!}{(s-2)!(k_1)!} \\ &= \sum_{k_1=0}^{k_s} \binom{s-2+k_1}{s-2} = \binom{s-1+k_1}{s-1} \end{aligned} \quad (2.26)$$

where the last identity is taken from Gradshteyn and Ryzhik.¹¹ Thus, (2.24) becomes

$$= \dots \sum_{k_s=0}^{P-m} \binom{s-1+k_1}{s-1} x_0^{k_s} \sum_{l=0}^{P-m-k_s} x_l^l \dots = \frac{1}{(s-1)!} \sum_{k_s=0}^{P-m} \frac{d^{s-1}}{dx_0^{s-1}} x_0^{k_s+s-1} \sum_{l=0}^{P-m-k_s} x_l^l \quad (2.27)$$

This indicates that there are m distinct x_{j_k} , each occurring s_{j_k} times. Evaluating (2.19) with

(2.27) gives

$$S(\{x_j\}, n, m, \{s_j\}) = \prod_{k=1}^m \left[\frac{1}{(s_{j_k} - 1)!} \frac{d^{s_{j_k}-1}}{dx_{j_k}^{s_{j_k}-1}} x_{j_k}^{s_{j_k}-1} \right] \sum_{l=1}^{m_s} \frac{x_{j_k}^{P-n+m-1}}{\prod_{i \neq l}^i (x_{j_l} - x_{j_i})} \quad (2.28)$$

When the derivatives in (2.28) are evaluated recursively, the final expression for the partition function is

$$Q(P) = \sum_j x_j^P + \sum_{n=2}^P \frac{P}{n} \left(\prod_{i=1}^n \sum_{j_i} \right) \times \left(\prod_{k=1}^n t_{j_k, j_{k+1}} \right) S(\{x_j\}, n, m, \{s_j\}) \quad (2.29)$$

Considering non-fixed atomic positions

Equation (2.29) is the result when considering fixed atomic positions. The addition of geometric degrees of freedom is fairly straightforward.⁷ In the Born-Oppenheimer approximation, Q is given by

$$Q = \int d\mathbf{R}^N \sum_j \langle j | \exp(-\beta H(\mathbf{R}^N)) | j \rangle \quad (2.30)$$

where there are N atoms, N_e electrons, and $\{|j\rangle\}$ is a set of electron orbitals. Each electron orbital is expressed as an anti-symmetrized product of one-electron orthonormal spin-orbitals such that

$$|j\rangle = A(\phi_{j1}, \alpha_{j1}, \phi_{j2}, \alpha_{j2}, \dots, \phi_{jN_e}, \alpha_{jN_e}) \quad (2.31)$$

The spatial orbitals ϕ can be expressed in terms of a set of atom-centered orbitals $\{|\chi_i\rangle\}$.

$$|\phi_j\rangle = \sum_i c_{ij} |\chi_i\rangle \quad (2.32)$$

For Hartree-Fock orbitals, at any given geometry an orbital will be a unitary transformation of an arbitrary starting set of orbitals $\{|\chi_i\rangle\}$

$$|\phi_k^{HF}\rangle = \sum_j U_{jk}^{HF} |\phi_j^0\rangle \quad (2.33)$$

$$|j^{HF}\rangle = A(\phi_{j1}^{HF}, \alpha_{j1}, \phi_{j2}^{HF}, \alpha_{j2}, \dots, \phi_{jN_e}^{HF}, \alpha_{jN_e}) \equiv |U^{HF} j^0\rangle \quad (2.34)$$

From (2.34), it can be generalized that an arbitrary unitary transformation is $|j\rangle = |Uj^0\rangle$. Noting that the trace of a matrix is invariant with respect to unitary transformations,¹³

$$\begin{aligned} Q &= \int d\mathbf{R}^N \sum_j \langle j^0 | \exp(-\beta H(\mathbf{R}^N)) | j^0 \rangle \\ &\propto \int d\mathbf{R}^N \sum_j \langle Uj^0 | \exp(-\beta H(\mathbf{R}^N)) | Uj^0 \rangle \end{aligned} \quad (2.35)$$

The proportionality constant is dependent on the number of possible unitary transforms.

If the Hartree-Fock-like approximation is made

$$\langle j | \exp(-\beta H(\mathbf{R}^N)) | k \rangle \approx \exp(-\beta H(\mathbf{R}^N)) \delta_{j,k} \quad (2.36)$$

then (2.35) becomes

$$Q_{HF} \propto \int d\mathbf{R}^N \sum_U \sum_{j^0} \exp[-\beta H(\mathbf{R}^N)_{Uj^0, Uj^0}] \quad (2.37)$$

Thus, the Hartree-Fock approximation removes electron-electron correlation. However, it is desirable to include not only the geometric degrees of freedom but also electron-electron correlation. So, writing the Born-Oppenheimer approximation in terms of the KBPI formalism gives

$$\begin{aligned} Q(P) &= \int d\mathbf{R}^N \left\{ \sum_j x_j^P(\mathbf{R}^N) + \sum_{n=2}^P \frac{P}{n} \left(\prod_{i=1}^n \sum_{j_i} \right) \left(\prod_{k=1}^n t_{j_k, j_{k+1}}(\mathbf{R}^N) \right) \right. \\ &\quad \times \sum_{l=1}^{m_s} \left[\frac{1}{(s_{j_l} - 1)!} \frac{d^{s_{j_l}-1}}{dx_{j_l}^{s_{j_l}-1}} \right] \frac{x_{j_l}^{P-1}}{\prod_{i \neq l} (x_{j_i}(\mathbf{R}^N) - x_{j_i}(\mathbf{R}^N))^{s_{j_l}}} \Big\} \end{aligned} \quad (2.38)$$

In moving forward, consider two assumptions: (1) the most important paths with two kinks consist of alternating ground and excited states and (2) the lowest energy state is non-degenerate.

Let n be the number of times the lowest energy state appears. Then (2.38) becomes

$$\begin{aligned}
Q(P) &= \int d\mathbf{R}^N \left\{ x_0^P + 2 \sum_{n=1}^{P/2} \frac{P}{2n(n-1)!} \frac{d^{n-1}}{dx_0^{n-1}} x_0^{P-1} \sum_{n_1=0}^m \sum_{n_2=0}^m \dots \binom{n}{n_1 n_2 \dots} \prod_j \left(\frac{t_{0j}^2}{(x_0 - x_j)} \right)^{n_j} \right\} \\
&= \int d\mathbf{R}^N \left\{ x_0^P + \sum_{m=1}^{P/2} \frac{P}{n!} \frac{d^{m-1}}{dx_0^{m-1}} x_0^{P-1} \sum_j \left(\frac{t_{0j}^2}{(x_0 - x_j)} \right)^n \right\} \\
&= \int d\mathbf{R}^N \left\{ x_0^P + \sum_{m=1}^{P/2} \frac{P}{n!} \frac{d^{m-1}}{dx_0^{m-1}} x_0^{P-1} \Gamma_0^m \right\} \\
&= \int d\mathbf{R}^N \left\{ x_0^P + \sum_{n=1}^{P/2} \frac{P}{n!} \sum_{m=0}^{n-1} \binom{n-1}{m} \frac{(P-1)! x_0^{P-n+m}}{(P-n+m)!} \frac{d^m}{dx_0^m} \Gamma_0^n \right\} \tag{2.39}
\end{aligned}$$

The binomial factor accounts for the number of different configurations the excited states can appear in the path, and the factor of two comes from the choice of the state being in either the ground or excited state.

It can be empirically shown that the most important term in (2.39) in the sum over m is the $m = 0$ term. The ratio of the $m = 1$ to $m = 0$ is

$$\frac{(n-1)x_0 n \Gamma_1}{(P-n+1)\Gamma_0} \tag{2.40}$$

Where

$$\Gamma_1 \equiv \frac{d}{dx_0} \Gamma_0 = - \sum_j \left(\frac{t_{0j}}{x_0 - x_j} \right)^2 \tag{2.41}$$

For small ε , (2.5) and (2.6) can be approximated to the second-order expansion of the exponent

$$\begin{aligned}
x_0 &= \langle 0 | \exp(-\varepsilon H) | 0 \rangle \approx 1 - \varepsilon E_0 \\
t_{0j} &= \langle 0 | \exp(-\varepsilon H) | 0 \rangle \approx -\varepsilon H_{0j} \\
\Gamma_0 &\approx \varepsilon \sum_j \left(\frac{H_{0j}^2}{E_0 - E_j} \right)^2 = -\varepsilon \Delta E_{MP2} \\
|\Gamma_1 / \Gamma_0| &\approx \frac{1}{\varepsilon \Delta E} \\
\frac{(n-1)x_0 n \Gamma_1}{(P-n+1)\Gamma_0} &\approx \frac{n(n-1)}{\beta \Delta E}
\end{aligned} \tag{2.42}$$

where ΔE_{MP2} is the MP2 correction to the Hartree-Fock energy and ΔE represents a typical difference in energy between the lowest energy state and one of the excited states appearing the sum for Γ_0 . Typically $\beta \Delta E \gg 1$, thus it is shown in (2.42) that the greatest contribution to (2.39) is the $m = 0$ term.

Evaluating (2.39) at the $m = 0$ gives

$$Q^{(0)} = \int d\mathbf{R}^N \left\{ x_0^P + \sum_{n=1}^{P/2} \binom{P}{n} x_0^{P-n} \Gamma_0^n \right\} \approx \int d\mathbf{R}^N \{ (x_0 + \Gamma_0)^P \} \tag{2.43}$$

where it is assumed that the sum on n converges quickly so that the sum can be extended from $P/2$ to P . For small ε ,

$$Q^{(0)} \approx \int d\mathbf{R}^N \{ [1 - \varepsilon(E_0 + \Delta E_{MP2})]^P \} \tag{2.44}$$

$$\langle E \rangle = -\frac{\partial \ln Q}{\partial \beta} \approx \langle E_0 + \Delta E_{MP2} \rangle_{\mathbf{R}^N} = \langle E_{MP2} \rangle_{\mathbf{R}^N} \tag{2.45}$$

where the subscripts indicate we are averaging over the geometric degrees of freedom. Thus, from (2.45), it is shown that if only the $m = 0$ term for paths of alternating ground and excited states are considered then the energy result should be the same as the MP2-level result.

Equation (2.45) is only useful if the initial guess for the lowest energy state corresponds to a Hartree-Fock solution for the given geometry. If this is not the case, then it becomes

necessary to extend (2.39) for $m > 0$. By examining (2.39), this case will include Γ_1 , the first derivative of Γ_0 , and higher order derivatives of Γ_0 . However, it has been shown that larger corrections to (2.45) include only Γ_1 terms.⁸ Though a more general formula including all possible Γ_m and m order derivatives, for convenience only derivatives up to the second order are included. So under these considerations, (2.39) becomes

$$\begin{aligned}
Q^{(1)} &= \int d\mathbf{R}^N \left\{ x_0^P + \sum_{n=1}^{P/2} \frac{P}{n!} \sum_{m=0}^{n-1} \binom{n-1}{m} \frac{(P-1)! x_0^{P-n+m}}{(P-n+m)!} \frac{n! \Gamma_0^{n-m} \Gamma_1^m}{(n-m)!} \right\} \\
&= \int d\mathbf{R}^N \left\{ x_0^P + \sum_{n=1}^{P/2} \frac{P}{n!} \sum_{k=0}^{n-1} \binom{n-1}{k} \frac{(P-1)! x_0^{P-1-k}}{(P-n-k)!} \frac{n! \Gamma_0^{k+1} \Gamma_1^{n-1-k}}{(k+1)!} \right\} \\
&= \int d\mathbf{R}^N \left\{ x_0^P + \sum_{k=0}^{P/2-1} \sum_{n=k+1}^{P/2} \frac{P!(n-1)! x_0^{P-1-k} \Gamma_0^{k+1} \Gamma_1^{n-1-k}}{k!(n-1-k)!(P-n-k)!(k+1)!} \right\} \\
&= \int d\mathbf{R}^N \left\{ x_0^P + \sum_{k=1}^{P/2-1} \sum_{n=0}^{P/2-k-1} \frac{P!(n+k)! x_0^{P-1-k} \Gamma_0^{k+1} \Gamma_1^n}{k!n!(P-1-k)!(k+1)!} \right\}
\end{aligned} \tag{2.46}$$

Using the following approximation

$$\sum_{n=0}^{P/2-k-1} \frac{(n+k)! \Gamma_1^n}{n!} = \frac{d^k}{d\Gamma_1^k} \sum_{n=0}^{P/2-k-1} \Gamma_1^{n+k} \approx \frac{d^k}{d\Gamma_1^k} \sum_{n=0}^{\infty} \Gamma_1^{n+k} = \frac{k!}{(1-\Gamma_1)^{k+1}} \tag{2.47}$$

Equation (2.46) becomes

$$Q^{(1)} = \int d\mathbf{R}^N \left\{ x_0^P + \sum_{k=1}^{P/2} \binom{P}{k} x_0^{P-k} \left(\frac{\Gamma_0}{1-\Gamma_1} \right)^k \right\} \approx \int d\mathbf{R}^N \left\{ \left(x_0 + \frac{\Gamma_0}{1-\Gamma_1} \right)^P \right\} \tag{2.48}$$

The above approach can be generalized to paths including more than one excited state between each occurrence of the lowest energy state. Henceforth, an *excursion* is the portion of the path between two occurrences of the ground state energy. An excursion contains one or more excited states. A weighting function can be developed to associate the lowest energy dominated (LED) set of paths with a particular excursion j . The weighting function is

$$w_j \equiv \frac{t_{0a} t_{0a} \dots t_{z0}}{(x_0 - x_a)(x_0 - x_b) \dots (x_0 - x_z)} \quad (2.49)$$

where the excursion j is defined to include the excited states a, b, \dots, z . Then

$$\mathcal{Q}_{LED} = \int d\mathbf{R}^N \left\{ x_0^P + 2 \sum_{n=1}^{P/2} \frac{P}{(n-1)!} \frac{d^{n-1}}{dx_0^{n-1}} x_0^{P-1} \sum_{n_1} \sum_{n_2} \dots \binom{n}{\{n_j\}} \prod_j w_j^{n_j} \frac{\delta_{n, \sum_j n_j}}{2n + \Delta n(\{n_j\})} \right\} \quad (2.50)$$

where $2n + \Delta n(\{n_j\})$ is the number of kinks for a particular set of excursions. If the initial states are well chosen, then the contributions from excursions with greater than one excited state per excursion should be much less than the contributions from the one excited state per excursion set of paths. That is, the following approximation can be considered

$$\frac{1}{2n + \Delta n(\{n_j\})} \approx \frac{1}{2n} \quad (2.51)$$

Therefore, (2.50) is rewritten as

$$\mathcal{Q}_{LED} \approx \int d\mathbf{R}^N \left\{ x_0^P + \sum_{n=1}^{P/2} \frac{P}{n!} \frac{d^{n-1}}{dx_0^{n-1}} x_0^{P-1} \Gamma_0^n \right\} \quad (2.52)$$

where

$$\Gamma_0 = \sum_j \frac{t_{oj}^2}{x_0 - x_j} + \sum_{j \neq k} \frac{t_{0j} t_{jk} t_{0k}}{(x_0 - x_j)(x_0 - x_k)} + \dots \quad (2.53)$$

Equation (2.53) can be rewritten with the following matrix identifications.

$$(W_0)_{ij} = \frac{t_{0i} t_{0j}}{\sqrt{(x_0 - x_i)(x_0 - x_j)}} \quad (2.54)$$

$$(M_0)_{ij} = \frac{t_{ij}}{\sqrt{(x_0 - x_i)(x_0 - x_j)}} (1 - \delta_{i,j}) \quad (2.55)$$

$$\Gamma_0 = \text{Tr}(W_0 + W_0 \cdot M_0 + W_0 \cdot M_0 \cdot M_0 + \dots) = \text{Tr}(W_0 + (I - M_0)^{-1}) \quad (2.56)$$

To infinite order, this sums all possible excursions from the lowest energy state with the provision that the contributions from excursions with different numbers of states is a rapidly decreasing function of the number of states involved in the excursion. With

$$\Gamma_1 = \frac{d}{dx_0} \Gamma_0 = \text{Tr}(W_1 + (I - M_1)^{-1}) \quad (2.57)$$

Equation (2.52) becomes

$$\mathcal{Q}_{LED} = \int d\mathbf{R}^N \left\{ \left(x_0 + \frac{\Gamma_0}{1 - \Gamma_1} \right)^P \right\} \propto \int d\mathbf{R}^N \left\{ \left(x_0(U) + \frac{\Gamma_0(U)}{1 - \Gamma_1(U)} \right)^P \right\} \quad (2.58)$$

This is the kink-based path integral (KBPI) formulation to quantum calculations.

Computing the Kink-Based Path Integral: An Adaptive Approach

The kink-based path integral formalism can be numerically solved using Monte Carlo integration. Monte Carlo integration allows sampling of the geometric degrees of freedom and electronic degrees of freedom as well as the kinks. An adaptive approach can be constructed such that the initial states are obtained using a Monte Carlo simulation. Then, the different N -electron states which appear during the simulation are used to update the estimates of the ground and excited states. Therefore, the estimates for the ground and excited states evolve according to the statistical sampling of the different N -electron states.

Optimizing the Monte Carlo

First, let us revisit the result of the previous chapter.

$$Q_{LED} = \int d\mathbf{R}^N \left\{ \left(x_0 + \frac{\Gamma_0}{1 - \Gamma_1} \right)^P \right\} \propto \int d\mathbf{R}^N \left\{ \left(x_0(U) + \frac{\Gamma_0(U)}{1 - \Gamma_1(U)} \right)^P \right\} \quad (3.1)$$

Equation (3.1) shows that the partition function is related to the ground and excited states. These states could be very large in number and thus computationally taxing to solve with a Monte Carlo algorithm. Secondly, as noted previously, a completely exhaustive sampling would be inefficient since only a subset of the states will contribute significantly to the partition function. Therefore, it is desirable to develop a Monte Carlo sampling procedure that will limit the number of excited states used to those with significant contributions to the partition function.

Label the excited states in order of decreasing magnitude of $[t_{0j}^2/(x_0 - x_j)]$, or approximately an excited state's contribution to the MP2 energy. Then, divide the excited states into groups of N_g states where group 1 corresponds to excited state 1 ... N_g , group corresponds to

excited states $N_g + 1 \dots 2N_g$, etc. If there are M_g such groups and letting $Q_{LED}(n_g)$ be the result using only the first n_g groups of excited states, Q_{LED} becomes

$$\begin{aligned}
Q_{LED} &= Q_{LED}(M_g) \\
&= Q_{LED}(M_g) - Q_{LED}(M_g - 1) + Q_{LED}(M_g - 1) \\
&= [Q_{LED}(M_g) - Q_{LED}(M_g - 1)] + [Q_{LED}(M_g - 1) - Q_{LED}(M_g - 2)] + \\
&\quad \dots + [Q_{LED}(1) - Q_{LED}(0)] + Q_{LED}(0) \\
&\equiv \Delta Q_{LED}(M_g) + \Delta Q_{LED}(M_g - 1) + \dots \Delta Q_{LED}(1) + \Delta Q_{LED}(0) \\
&= \sum_{j=0}^{M_g} \Delta Q_{LED}(j)
\end{aligned} \tag{3.2}$$

Thus, j can be sampled during a Monte Carlo procedure. For reasonably ordered states, this summation ought to converge for relatively small j and the matrices involved in evaluating $\Delta Q_{LED}(j)$ are manageable.

Equations (2.56) and (2.57) involves the matrix inversion $(I - M_0)^{-1}$. Matrix inversions scale \mathbf{K}^3 in the dimension of matrix \mathbf{K} .¹³ This computational obstacle can be overcome by replacing the inversion step with a matrix multiplication.

First, rewrite equation (2.54)

$$(W_0)_{ij} = \frac{t_{0i}t_{0j}}{\sqrt{(x_0 - x_i)(x_0 - x_j)}} = \left(\frac{t_{0i}}{\sqrt{(x_0 - x_i)}} \right) \left(\frac{t_{0j}}{\sqrt{(x_0 - x_j)}} \right) \equiv f_{0i}f_{0j} \tag{3.3}$$

Equation (2.56) becomes

$$\Gamma_0 = \mathbf{f}_0 \bullet (\mathbf{I} + \mathbf{M}_0 + \mathbf{M}_0 \cdot \mathbf{M}_0 + \dots) \cdot \mathbf{f}_0 = \mathbf{f}_0 \cdot \mathbf{f}_0 + \mathbf{f}_0 \cdot \mathbf{f}_1 + \mathbf{f}_0 \cdot \mathbf{f}_2 + \dots = \mathbf{f}_0 \cdot (\mathbf{f}_0 + \mathbf{f}_1 + \dots) \tag{3.4}$$

where

$$\mathbf{f}_n \equiv \mathbf{M}^n \cdot \mathbf{f}_0 = \mathbf{M}_0 \cdot \mathbf{f}_{n-1} \tag{3.5}$$

Therefore, Γ_0 can be generated iteratively until a convergence tolerance is reached. Convergence is only guaranteed when \mathbf{M}_0 is positive, as is the case in most physical systems. A similar treatment is applied to equation (2.57)

$$\Gamma_1 = \frac{d}{dx_0} \Gamma_0 = \mathbf{g}_0 \cdot (\mathbf{f}_0 + \mathbf{f}_1 + \dots) + \mathbf{f}_0 \cdot (\mathbf{g}_0 + \mathbf{g}_1 + \dots) \quad (3.5)$$

where

$$\mathbf{g}_0 \equiv \frac{d}{dx_0} \mathbf{f}_0 \quad (3.6)$$

$$\mathbf{g}_n = \mathbf{f}_{n-1} \cdot \frac{d}{dx_0} \mathbf{M}_0 + \mathbf{g}_{n-1} \cdot \mathbf{M}_0 \quad (3.7)$$

Under these conditions, the energy estimator is obtained

$$\begin{aligned} E_{est} &= -\frac{d}{d\beta} \left(x_0 + \frac{\Gamma_0}{1-\Gamma_1} \right)^P \\ &= \frac{1}{P} \frac{d}{d\varepsilon} \left(x_0 + \frac{\Gamma_0}{1-\Gamma_1} \right)^P \\ &= -\left(x_0 + \frac{\Gamma_0}{1-\Gamma_1} \right)^P \left[\frac{x'_0 + \Gamma'_0/(1-\Gamma_1) + \Gamma_0 \Gamma'_1/(1-\Gamma_1)^2}{x_0 + \Gamma_0/(1-\Gamma_1)} \right] \end{aligned} \quad (3.8)$$

where the primes denote differentiation with respect to ε .

The series for Γ_0 , Γ_1 , and the energy estimator are alternating series. These could pose a potential computational challenge.¹³ The following relation to determine convergence was established as workable based off previous studies

$$\mathbf{I} = (\mathbf{I} - \mathbf{M}_0) \cdot (\mathbf{I} - \mathbf{M}_0)^{-1} \quad (3.9)$$

$$\mathbf{f}_0 \cdot \mathbf{I} \cdot \mathbf{f}_0 \equiv \mathbf{f}_0 \cdot (\mathbf{I} - \mathbf{M}_0) \cdot (\mathbf{I} - \mathbf{M}_0)^{-1} \cdot \mathbf{f}_0 \quad (3.10)$$

$$f_0^2 = (\mathbf{f}_0 - \mathbf{f}_1) \cdot (\mathbf{f}_0 + \mathbf{f}_1 + \mathbf{f}_2 + \dots) \quad (3.11)$$

Thus, a specific convergence tolerance can be specified for (3.11) such that when reached the iterative procedure is truncated.

Roundoff error can be numerically avoided as follows. Since x_j and t_{ij} are directly proportional to ε , then it follows that

$$\mathbf{f}_n = \sqrt{\varepsilon} \hat{\mathbf{f}}_0$$

$$\mathbf{g}_n = \frac{1}{\sqrt{\varepsilon}} \hat{\mathbf{g}}_0 \quad (3.12)$$

$$\frac{d}{dx_0} \mathbf{M}_0 \equiv \mathbf{M}'_0 = \frac{1}{\varepsilon} \mathbf{M}'_0 \quad (3.13)$$

$$\Gamma_0 = \hat{\mathbf{f}}_0 \cdot \sum_n \hat{\mathbf{f}}_n \quad (3.14)$$

$$\Gamma_1 = \hat{\mathbf{g}}_0 \cdot \sum_n \hat{\mathbf{f}}_n + \hat{\mathbf{f}}_0 \cdot \sum_n \hat{\mathbf{g}}_n \quad (3.15)$$

$$\Gamma'_0 = \hat{\mathbf{f}}'_0 \cdot \sum_n \hat{\mathbf{f}}_n + \hat{\mathbf{f}}_0 \cdot \sum_n \hat{\mathbf{f}}'_n \quad (3.16)$$

$$\Gamma_1 = \left[\hat{\mathbf{g}}'_0 \cdot \sum_n \hat{\mathbf{f}}_n + \hat{\mathbf{f}}'_0 \cdot \sum_n \hat{\mathbf{g}}_n + \hat{\mathbf{g}}_0 \cdot \sum_n \hat{\mathbf{f}}'_n + \hat{\mathbf{f}}_0 \cdot \sum_n \hat{\mathbf{g}}'_n \right] \quad (3.17)$$

Sampling the Monte Carlo

Sampling unitary transformations U was accomplished in the following way. Two orbitals ϕ_j and ϕ_i were randomly chosen from the list of single particle orbitals. A new pair of orbitals was formed via a simple unitary transformation

$$\phi'_j = \phi_j \cos \theta + \phi_i \sin \theta \quad (3.19)$$

$$\phi'_i = -\phi_j \sin \theta + \phi_i \cos \theta \quad (3.20)$$

with θ sampled randomly from 0 to 2π .

In previous work only single and double "excitations" from the ground state were considered as candidates for kinks.⁵⁻⁷ That is, the difference between the ground state and an allowed excited state is the transfer of one or two electrons from occupied orbitals to unoccupied orbitals. The following scheme was therefore used for addition and removal of kinks. After sampling the rotations during the first Monte Carlo pass, the ground state was identified and

remained unchanged during the simulation. A list of states corresponding to double and single excitations was constructed and used for the remainder of the simulation. A value of $N_g = 10$ was used and at each Monte Carlo pass included an attempt to increase or decrease by 1 the value j in (3.2).

Lastly, each Monte Carlo pass included an attempt to move each atom in turn, as in a standard Monte Carlo simulation. When an atom move was attempted, the single particle states were no longer orthogonal; the orbitals were orthonormalized using the Gram-Schmidt method.¹⁶

Application of KBPI to Boron and Boron Mono-nitrogen Clusters

The adaptive KBPI method was applied to small boron and mono-nitrogen-substituted boron clusters. The full intention is to study the geometric and electronic structure of the clusters. The electron affinities were obtained by studying the anion, cation, and neutral forms of the clusters.

Introduction

The electron affinity is the energy required to adiabatically detach an electron from a chemical species. That is,



It can be determined by subtracting the total energy of the anionic species from the total energy of the neutral species. The electron affinity for the cation can also be determined similarly.

The clusters studied were B_n and $B_{n-1}N$ where n is 2, 3, and 4. A previous DFT study has identified the different semi-stable isomers for these clusters.¹⁶ Figure 1 reproduces these geometries.

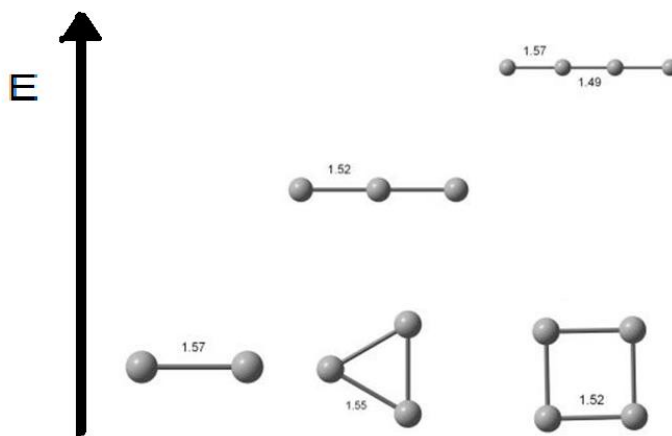


Figure 1. The different isomers of boron clusters being studied

The KBPI method is best suited to study the geometry at the global minima. Therefore, it is expected for the KBPI method to return the geometric results of the lowest energy isomer from the DFT studies.

Method

The basis functions used in this study were from the 6-31G basis set.¹⁷ The basis set was orthonormalized in GAMESS, giving an initial guess of the ground state energies.¹⁸ Previous work has indicated that only the 0-kink and 2-kink contribute significantly to partition function, and therefore to conserve computational resources this study only considered 0 and 2 kinks in the path.⁵⁻⁷ Each simulation ran for 5,000 Monte Carlo passes. In general, it was found that the energy estimate converged between 2,000 and 2,500 passes. The statistical inefficiency was calculated for each Monte Carlo simulation.¹⁹ In general, it indicated fast convergence with most of the Monte Carlo passes contributing significantly to the final estimate.

Results

The total energy was determined for each cluster and is given in Table 1. Also in Table 1 are the average bond lengths and angle between bonds and the electron affinities for the neutral and cation species.

Cluster	Total Energy (Hartrees)	Electron Affinity (Hartrees)	Average Bond Length (Å)	Average Angle	Relative Geometry
B ₂ ⁻	-81.3652 ₄	0.002 ₄	1.57 ₁	180°	Linear
B ₂	-81.3672 ₄		1.57 ₁	180°	Linear
B ₂ ⁺	-81.1981 ₆		1.57 ₁	180°	Linear
B ₃ ⁻	-79.5413 ₄	0.005 ₄	1.55 ₁	60°	Trigonal
B ₃	-79.5465 ₅	0.004 ₅	1.55 ₁	60°	Trigonal
B ₃ ⁺	-79.5896 ₄		1.55 ₁	60°	Trigonal
B ₄ ⁻	-75.3492 ₆	0.009 ₆	1.52 ₁	90°	Square
B ₄	-75.3578 ₂	0.011 ₂	1.52 ₁	90°	Square
B ₄ ⁺	-75.3692 ₃		1.52 ₁	90°	Square
BN ⁻	-79.0431 ₄	0.003 ₅	1.47 ₁	180°	Linear
BN	-79.0456 ₅	0.041 ₄	1.47 ₁	180°	Linear
BN ⁺	-79.0869 ₄		1.47 ₁	180°	Linear
B ₂ N	-74.0452 ₅	0.018 ₆	1.45 ₁	60°	Trigonal
B ₂ N	-74.0632 ₆	0.040 ₁	1.45 ₁	60°	Trigonal
B ₂ N ⁺	-74.1034 ₁		1.45 ₁	60°	Trigonal
B ₃ N ⁻	-63.0134 ₈	0.002 ₈	1.43 ₁	107°	Tetrahedral
B ₃ N	-63.0156 ₈	0.007 ₉	1.43 ₁	107°	Tetrahedral
B ₃ N ⁺	-63.0230 ₉		1.42 ₁	117.5°	Trigonal pyramidal

Table 1. The data for each cluster. Subscripts represent statistical error.

Discussion

From Table 1, it is easy to discern which electronic structure is preferred. For diatomic boron, B₂ neutral is preferred. According to classical molecular orbital theory, in B₂ all of the molecular orbitals are occupied. Removing an electron from the diatomic is thus energetically unfavorable since the removal would disrupt the symmetry of the orbitals. This is why the energy required to remove the electron is large in comparison to the anionic diatomic. Other similar trends can be explained for the other clusters. Since the adiabatic detachment of an electron indicates a pattern expected from considering molecular orbital theory, it is shown from this study that the bonding nature of boron clusters is dominated by covalent interaction.

For geometries, it is worth noting that our results for boron clusters correlate very well with a previous DFT study.¹⁶ For the boron mono-nitrogen clusters, there is one interesting result. According to Table 1, B₃N clusters prefer to possess tetrahedral geometries as opposed to planar geometries. This so-called “caging” can be attributed to the electronegativity of nitrogen versus boron. The neutral B₃N forms the tetrahedral. The anion carries the extra electron on the

borons through resonance. The cation removes an electron from the nitrogen. This free radical is more trigonal pyramidal due to the free radical's interaction with the B-N bonds. That is, from valence shell electron pair repulsion theory, the free radical does not repel the covalent B-N bond enough to force a tetrahedral geometry.

Conclusion

The adaptive KBPI method has been applied to boron and boron mono-nitrogen clusters. The results found can be explained using descriptions borrowed from simple molecular orbital theory, thus indicating boron and boron mono-nitrogen clusters to be dominated by mostly covalent interactions.

Afterword/Acknowledgements

The complete derivation of a kink-based approach to quantum mechanics and an adaptive approach to its calculation has been applied to simple boron and boron mononitride clusters in this work. This work was but a small part of an on-going project to extend the application of the adaptive KBPI method to larger electronic systems with the dominate interaction between constituents being van der Waal interactions. This is the main motivation driving the development of the KBPI method.

All of the simulations in this communication were completed on computers in the High Performance Computing facility at Louisiana State University. This project was funded by a grant from the Tiger Athletic Foundation.

I would like to thank the following individuals. Cheri McFerrin, who taught me how to use the software packages used in analyzing the data. Gyun-Tack Bae, who instructed me on how to access the supercomputing facilities. Matt McKenzie and Samuel Kasler, for many mornings of coffee and interesting conversation. Bin Chen for some recommendations on convergence parameters for the Monte Carlo simulations. The faculty and staff of the Honors College at LSU for their patience in answering my many questions about the thesis project. My family and friends for motivational support. And finally, my thesis advisor, Randall Hall, for dealing with my ignorance and naivety for three years and for giving me the opportunity to study under him.

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