$\hat{O}=\hat{F}\hat{G}=$ product of operators $\hat{F}$ and $\hat{G}$ with matrix elements $F\left(\underline{R},\underline{R}'\right)$ and $G\left(\underline{R},\underline{R}'\right)$. What is $O\left(\underline{R},\underline{R}'\right)$?

$$\hat{O}\psi\left(\underline{R}\right)=\int_{V^N}O\left(\underline{R},\underline{R}'\right)\psi\left(\underline{R}'\right)d\underline{R}'=\hat{F}\underbrace{\hat{G}\psi\left(\underline{R}\right)}_{\int_{V^N}G\left(\underline{R},\underline{R}'\right)\psi\left(\underline{R}'\right)d\underline{R}'}$$

$$=\hat{F}\int_{V^N}G\left(\underline{R},\underline{R}'\right)\psi\left(\underline{R}'\right)d\underline{R}'$$

$$=\int_{V^N}\underbrace{\left[\hat{F}_{\underline{R}}G\left(\underline{R},\underline{R}'\right)\right]}_{\int_{V^N}\left[F\left(\underline{R},\underline{R}''\right)\right]G\left(\underline{R}'',\underline{R}'\right)d\underline{R}''}\psi\left(\underline{R}'\right)d\underline{R}'$$

$$=\int_{V^N}\left\{\int_{V^N}F\left(\underline{R},\underline{R}''\right)G\left(\underline{R}'',\underline{R}'\right)d\underline{R}''\right\}\psi\left(\underline{R}'\right)d\underline{R}'$$

$$=\int_{V^N}O\left(\underline{R},\underline{R}'\right)\psi\left(\underline{R}'\right)d\underline{R}'$$

$$\rightarrow O\left(\underline{R},\underline{R}'\right)=\int_{V^N}F\left(\underline{R},\underline{R}''\right)G\left(\underline{R}'',\underline{R}'\right)d\underline{R}'' \quad (51)$$

for the product $\hat{O}=\hat{F}\hat{G}$. This is a convolution integral of $F\left(\underline{R},\underline{R}''\right)$ and $G\left(\underline{R}'',\underline{R}'\right)$.

For simplification of notation, set $\hat{U}=e^{-\beta\hat{H}}$, i.e. the unnormalized density operator. The unnormalized density matrix is

$$U\left(\underline{R},\underline{R}'\right)=ZW\left(\underline{R},\underline{R}'\right).$$

We can set

$$\hat{U}=e^{-q\beta\hat{H}}e^{-(1-q)\beta\hat{H}}.$$

The two operators in the exponentials commute, so we can combine the two exponentials.

$$\hat{U}=e^{-q\beta\hat{H}-\beta\hat{H}+q\beta\hat{H}}=e^{-\beta\hat{H}}$$

In general, $e^{\hat{F}+\hat{G}}\neq e^{\hat{F}}e^{\hat{G}}$ for non-commuting operators $\hat{F}$ and $\hat{G}$.

$$U\left(\underline{R},\underline{R}';\beta\right)=\int_{V^N}U\left(\underline{R},\underline{R}'';q\beta\right)U\left(\underline{R}'',\underline{R}';(1-q)\beta\right)d\underline{R}'' \quad (52)$$

$U\left(\underline{R},\underline{R}';\beta\right)$ are the matrix elements of $e^{-\beta\hat{H}}$, $U\left(\underline{R},\underline{R}'';q\beta\right)$ are the matrix elements of $e^{-q\beta\hat{H}}$ and $U\left(\underline{R}'',\underline{R}';(1-q)\beta\right)$ are the matrix elements of $e^{-(1-q)\beta\hat{H}}$.

For $0<q<1$,

$$q\beta=k_B^{-1}\frac{q}{T}=\frac{1}{k_BT_q},$$

where $T_q=\dfrac{T}{q}>T$, and

$$(1-q)\beta=k_B^{-1}\frac{1-q}{T}=\frac{1}{k_BT_{1-q}}$$

where $T_{1-q}=\dfrac{T}{1-q}>T$.

Equation 52 represents the matrix elements $U\left(\underline{R},\underline{R}';\beta\right)$ of $e^{-\beta\hat{H}}$ at temperature T in the form of a convolution of matrix elements $U\left(\underline{R},\underline{R}'';q\beta\right)$ of $e^{-q\beta\hat{H}}$ and $U\left(\underline{R}'',\underline{R}';(1-q)\beta\right)$ of $e^{-(1-q)\beta\hat{H}}$ at the higher effective temperatures T_q and T_{1-q}.

Apply equation 52 successively M times.

$$U(\underline{R},\underline{R}';\beta)=\int_{V^N}U\left(\underline{R},\underline{R}_1;\frac{\beta}{M+1}\right)U\left(\underline{R}_1,\underline{R}';\frac{M}{M+1}\beta\right)d\underline{R}_1$$

$$=\int_{V^N}\int_{V^N}U\left(\underline{R},\underline{R}_1;\frac{\beta}{M+1}\right)U\left(\underline{R}_1,\underline{R}_2;\frac{\beta}{M+1}\right)U\left(\underline{R}_2,\underline{R}';\frac{M-1}{M+1}\beta\right)d\underline{R}_1 d\underline{R}_2$$

$$=\int_{V^N}\int_{V^N}\int_{V^N}U\left(\underline{R},\underline{R}_1;\frac{\beta}{M+1}\right)U\left(\underline{R}_1,\underline{R}_2;\frac{\beta}{M+1}\right)$$

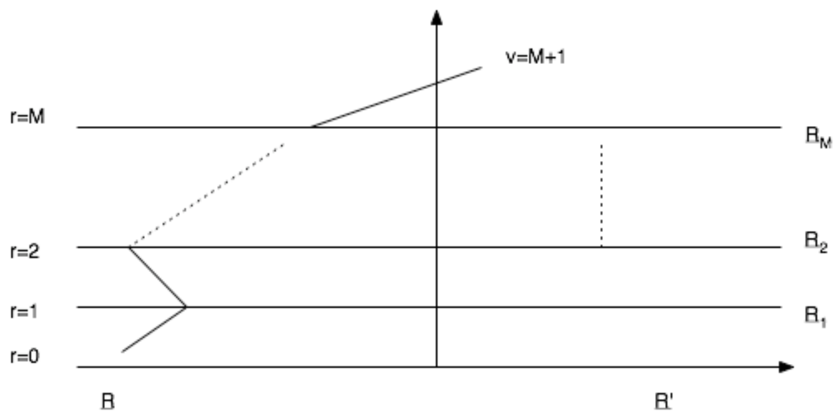
$$\times U\left(\underline{R}_2,\underline{R}_3;\frac{\beta}{M+1}\right)U\left(\underline{R}_3,\underline{R}';\frac{M-2}{M+1}\beta\right)d\underline{R}_1 d\underline{R}_2 d\underline{R}_3$$

Repeating this procedure M times yields

$$U(\underline{R},\underline{R}';\beta)=\int_{V^N}\dots\int_{V^N}\prod_{\nu=0}^{M}U\left(\underline{R}_\nu,\underline{R}_{\nu+1};\frac{\beta}{M+1}\right)d\underline{R}_1\dots d\underline{R}_M \quad (53)$$

This is a $3NM$-dimensional integration, with M integrations. By definition, $\underline{R}_0=\underline{R}$, and $\underline{R}_{M+1}=\underline{R}'$. $U(\underline{R},\underline{R}';\beta)$ is given here in terms of $U\left(\underline{R}_\nu,\underline{R}_{\nu+1};\frac{\beta}{M+1}\right)$ at the higher effective temperature $(M+1)T$.

Illustration:



For any $\underline{R}_1,\underline{R}_2,\dots,\underline{R}_M$ the set of M $3N-$dimensional configurations $\underline{R}_1,\underline{R}_2,\dots,\underline{R}_M$ may be thought of as a path, taken at the discrete imaginary time steps $\nu=1,2,\dots,M$ leading from the initial configuration $\underline{R}$ to the final configuration $\underline{R}'$. The intermediate configurations $\underline{R}_1,\underline{R}_2,\dots,\underline{R}_M$ are all integrated over all possible $3N-$dimensional configurations.

The M $3N-$dimensional integrations in equation 52 correspond to an integral over all discrete paths (at imaginary times $\nu=1,2,\dots,M$) connecting in $3N-$dimensional configuration space $\underline{R}$ and $\underline{R}'$. Equation 52 is the discrete imaginary time path integral representation of $U(\underline{R},\underline{R}';\beta)$ (Feynman path integral).

The purpose of all of this is to make M large enough so that one can insert the known high-temperature limit for $U\left(\underline{R}_\nu,\underline{R}_{\nu+1};\dfrac{\beta}{M+1}\right)$ at the effective temperature $(M+1)T$.

3.1 High-Temperature Limit of the Density Matrix

The Hamiltonian is the sum of the kinetic energy and the potential energy,

$$\hat{H}=\hat{T}+\hat{V}.$$

The equation

$$e^{-\beta\hat{H}}=e^{-\beta\hat{T}}e^{-\beta\hat{V}} \quad (54)$$

holds for $\beta<<1$.

$$U(\underline{R},\underline{R}')=\int_{V^N}F(\underline{R},\underline{R}'')G(\underline{R}'',\underline{R}')d\underline{R}''$$

Use equation (51), with $\hat{O}=e^{-\beta\hat{H}}=\hat{F}\hat{G}$, where here $\hat{F}=e^{-\beta\hat{T}}$ and $\hat{G}=e^{-\beta\hat{V}}$. $O(\underline{R},\underline{R}')=U(\underline{R},\underline{R}')$. $F(\underline{R},\underline{R}'')$ are the coordinate space matrix elements of $e^{-\beta\hat{T}}$, and $G(\underline{R}'',\underline{R}')$ are the coordinate space matrix elements of $e^{-\beta\hat{V}}$.

Using equation (48),

$$G(\underline{R}'',\underline{R}')=e^{-\beta\hat{V}_{\underline{R}''}}\delta(\underline{R}''-\underline{R}')=e^{-\beta V(\underline{R}'')}\delta(\underline{R}''-\underline{R}')$$

$$G(\underline{R}'',\underline{R}')=e^{-\frac{\beta}{2}(V(\underline{R}'')+V(\underline{R}'))}\delta(\underline{R}''-\underline{R}') \quad (55)$$

$$F(\underline{R},\underline{R}'')=e^{-\beta\hat{T}}\delta(\underline{R}-\underline{R}'')$$

Write $\delta(\underline{R}-\underline{R}'')$ in terms of the orthonormalized eigenfunctions of $\hat{T}$.

$$\hat{T}\psi(\underline{R})=-\sum_{i=1}^{N}\frac{\hbar^2}{2m}\nabla_i^2\psi(\underline{R})=T\psi(\underline{R})$$

For a sum of commuting one-body operators like $-\dfrac{\hbar^2}{2m}\nabla_i^2$ we have

$$\psi(\underline{R})=\phi_1(\underline{r}_1)\phi_2(\underline{r}_2)\ldots\phi_N(\underline{r}_N)$$

$$T=\sum_{i=1}^{N}T_i$$

$$\hat{T}_i\phi_i(\underline{r}_i)=-\frac{\hbar^2}{2m}\nabla_i^2\phi_i(\underline{r}_i)=T_i\phi_i(\underline{r}_i) \quad (56)$$

$$\psi(\underline{R})=\prod_{i=1}^{N}\phi_i(\underline{r}_i) \quad (57)$$

$$\hat{T}\psi(\underline{R})=\sum_{i=1}^{N}T_i\psi(\underline{R}) \quad (58)$$

$$\phi_i(\underline{r}_i)=\left(\frac{1}{2\pi}\right)^{3/2}e^{i\underline{k}_i\cdot\underline{r}_i} \quad (59)$$

where $\underline{k}_i=\left(k_i^x,k_i^y,k_i^z\right)$, any of which can assume values from $-\infty$ to $+\infty$.

$$\left(\frac{1}{2\pi}\right)^3\int e^{i(\underline{k}_i-\underline{k}_i')\underline{r}_i}d\underline{r}_i=\delta(\underline{k}_i-\underline{k}_i')$$

$$\psi_{\underline{k}}\left(\underline{R}\right)=\left(\frac{1}{2\pi}\right)^{3N/2}\prod_{i=1}^{N}e^{i\underline{k}_i\cdot\underline{r}_i}$$

where $\underline{k}=\left(\underline{k}_1,\underline{k}_2,...,\underline{k}_N\right)$

$$\int\psi_{\underline{k}}*\left(\underline{R}\right)\psi_{\underline{k}}\left(\underline{R}''\right)d\underline{k}=\delta\left(\underline{R}-\underline{R}''\right)$$

$$e^{-\beta\hat{T}_{\underline{R}}}\delta\left(\underline{R}-\underline{R}''\right)=\left(\frac{1}{2\pi}\right)^{3N}\int e^{-\beta\hat{T}_{\underline{R}}}e^{i\underline{k}\cdot\underline{R}}e^{-i\underline{k}\cdot\underline{R}''}d\underline{k}$$

$$=\left(\frac{1}{2\pi}\right)^{3N}\int e^{-\frac{\hbar^2\beta k^2}{2m}}e^{i\underline{k}\left(\underline{R}-\underline{R}''\right)}d\underline{k}$$

where $\underline{k}=\left(\underline{k}_1,\underline{k}_2,...,\underline{k}_N\right)$ and $k^2=\sum_{i=1}^{N}k_i^{\ 2}$. This is a 3N-dimensional Gaussian integral

$$F\left(\underline{R},\underline{R}''\right)=\left(\frac{m}{2\pi\beta\hbar^2}\right)^{3N/2}\exp\left\{-\frac{m}{2\beta\hbar^2}\left(\underline{R}-\underline{R}''\right)^2\right\}\quad(72)$$

$$U\left(\underline{R},\underline{R}'\right)=\left(\frac{m}{2\pi\beta\hbar^2}\right)^{3N/2}\exp\left\{-\frac{m}{2\beta\hbar^2}\left(\underline{R}-\underline{R}'\right)^2\right\}e^{-\frac{\beta}{2}\left[V\left(\underline{R}\right)+V\left(\underline{R}'\right)\right]}$$

This is the classical high-temperature limit of the density matrix elements $U\left(\underline{R},\underline{R}'\right)$.