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1. Basic Formal Concepts

We have N identical particles of mass m. Internal degrees of freedom and special extent are neglected. The position variable of particle i $(1 \le i \le N)$ in 3D space is $\underline{r}_i = (x_i, y_i, z_i)$. $\underline{R} = (\underline{r}_1, \underline{r}_2, ..., \underline{r}_N) = (x_1, y_1, z_1, ..., x_N, y_N, z_N)$ is a $3N$-dimensional vector which holds the position variables of all of the N particles in 3D space.

NB: We will always use right-handed frames of reference.

The gradient, or Nabla operator, of particle i is

$$\nabla_i = \left(\frac{\partial}{\partial x_i}, \frac{\partial}{\partial y_i}, \frac{\partial}{\partial z_i} \right).$$

Applied to a function, this will provide a 3D vector

$$\nabla_i f(..., \underline{r}_i, ...) = \left(\frac{\partial f}{\partial x_i}, \frac{\partial f}{\partial y_i}, \frac{\partial f}{\partial z_i} \right).$$

Equivalently,

$$\nabla_i f = \begin{pmatrix} \frac{\partial f}{\partial x_i} \\ \frac{\partial f}{\partial y_i} \\ \frac{\partial f}{\partial z_i} \end{pmatrix}.$$

The Laplace operator for particle i is

$$\nabla_i^2 = \nabla_i \cdot \nabla_i = \left(\frac{\partial}{\partial x_i}, \frac{\partial}{\partial y_i}, \frac{\partial}{\partial z_i} \right) \begin{pmatrix} \frac{\partial}{\partial x_i} \\ \frac{\partial}{\partial y_i} \\ \frac{\partial}{\partial z_i} \end{pmatrix} = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2},$$

where the dot represents the scalar product. This provides a scalar.

Applied to a function, this is

$$\nabla_i^2 f(..., \underline{r}_i, ...) = \frac{\partial^2 f}{\partial x_i^2} + \frac{\partial^2 f}{\partial y_i^2} + \frac{\partial^2 f}{\partial z_i^2}.$$

The relative position vector between two particles is

$$\underline{r}_{ij} = \underline{r}_i - \underline{r}_j = \begin{pmatrix} x_i - x_j \\ y_i - y_j \\ z_i - z_j \end{pmatrix},$$

which points from $\underline{r}_j$ to $\underline{r}_i$. The distance between these two particles is

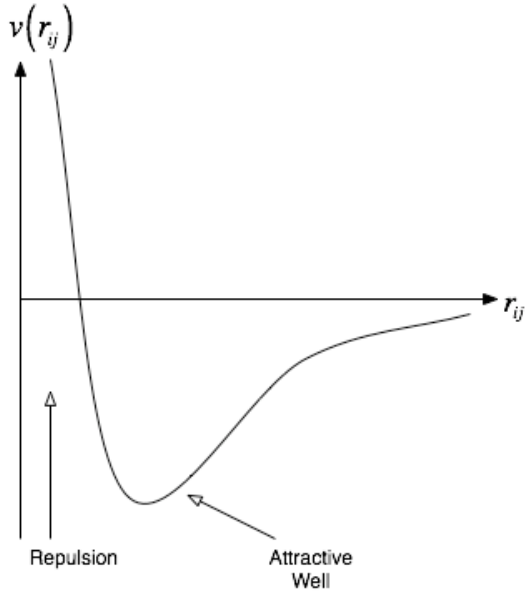
$$r_{ij} = \left|\underline{r}_i - \underline{r}_j\right| = \left|\underline{r}_{ij}\right| = \sqrt{\left(x_i - x_j\right)^2 + \left(y_i - y_j\right)^2 + \left(z_i - z_j\right)^2}$$

Every particle i interacts with every other particle $j \neq i$ via a central pairwise (only consider pairs of particles, i.e. 2-body interactions) central potential $v\left(r_{ij}\right)$, which depends only on the distance r_{ij} and not on the direction.

A typical 2-body potential $v\left(r_{ij}\right)$ is the Lennard-Jones potential

$$v\left(r_{ij}\right) = 4\varepsilon\left(\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right)$$

where the constants ε and σ depend on the material. This is used for rare gas elements He, Ne, Ar, Xe and H_2.

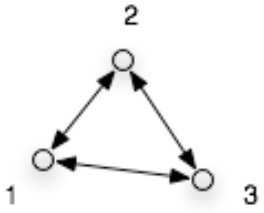


The operator $V\left(\underline{R}\right)$ of the internal potential energy is

$$V\left(\underline{R}\right) = \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} v\left(r_{ij}\right) = \sum_{i<j=1}^{N} v\left(r_{ij}\right) = \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1 \\ j\neq i}}^{N} v\left(r_{ij}\right) = \frac{1}{2}\sum_{i\neq j=1}^{N} v\left(r_{ij}\right) \qquad (1)$$

This is a sum over all distinct pairs of particles, where $i \neq j$ as a particle dos not interact with itself. The latter two have factors of a half as they count each interaction twice.

Example for $N = 3$:



$$V(\underline{R}) = \sum_{i=1}^{2}\sum_{j=i+1}^{3} v(r_{ij}) = v(r_{12}) + v(r_{13}) + v(r_{23})$$

$$V(\underline{R}) = \frac{1}{2}\sum_{i=1}^{3}\sum_{\substack{j=1 \\ j\neq i}}^{3} v(r_{ij}) = \frac{1}{2}\left(v(r_{12}) + v(r_{13}) + v(r_{21}) + v(r_{13}) + v(r_{31}) + v(r_{32})\right)$$

As $r_{ji} = \left|\underline{r}_j - \underline{r}_i\right| = \left|\underline{r}_i - \underline{r}_j\right| = r_{ij}$, $r_{21} = r_{12}$, $r_{31} = r_{13}$, $r_{32} = r_{23}$, and hence the potentials are the same in each case. Hence,

$$V(\underline{R}) = \frac{1}{2}\sum_{i=1}^{3}\sum_{\substack{j=1 \\ j\neq i}}^{3} v(r_{ij}) = v(r_{12}) + v(r_{13}) + v(r_{23})$$

So the factor $\frac{1}{2}$ in $V(\underline{R}) = \frac{1}{2}\sum_{i\neq j=1}^{N} v(r_{ij})$ is due to every distinct pair $\{i, j\}$ $(i \neq j)$ is contained twice in $\sum_{i\neq j=1}^{N} v(r_{ij})$.

Let $\psi(\underline{R}) = \psi(\underline{r}_1, \underline{r}_2, ..., \underline{r}_N)$ be the many-body wave function that depends on the coordinates $\underline{r}_1, \underline{r}_2, ..., \underline{r}_N$ of the N particles. To act with an operator $V(\underline{R})$ on $\psi(\underline{R})$ means that we multiply $\psi(\underline{R})$ with $V(\underline{R})$ to obtain the result $V(\underline{R})\psi(\underline{R})$. The operator of internal potential energy is an operator of multiplication with the total potential energy $V(\underline{R})$.

The operator $\hat{T}$ of the (non-relativistic) kinetic energy is classically $T = \sum_{i=1}^{N} \frac{p_i^2}{2m^2}$ where $p_i^2 = \underline{p}_i \cdot \underline{p}_i = p_i^{(x)2} + p_i^{(y)2} + p_i^{(z)2}$, where $\underline{p}_i = \left(p_i^{(x)}, p_i^{(y)}, p_i^{(z)}\right)$ is the three-dimensional linear momentum of particle i. We want to turn this into quantum mechanics, i.e. $T \to \hat{T}$. Replace $\underline{p}_i \to \hat{\underline{p}}_i = -i\hbar\nabla_i$ to get the momentum operator of particle i. $p_i^2 = \underline{p}_i \cdot \underline{p}_i \to \left(-i\hbar\nabla_i\right)\left(-i\hbar\nabla_i\right) = -\hbar^2\nabla_i^2$. Hence,

$$\hat{T} = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 = \sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m}\nabla_i^2\right) = \sum_{i=1}^{N}\frac{\hat{\underline{p}}_i^{\,2}}{2m}. \qquad (2)$$

$\frac{\hat{\underline{p}}_i^{\,2}}{2m} = -\frac{\hbar^2}{2m}\nabla_i^2$ is the operator of the kinetic energy of particle i.

NB: $\hbar = \frac{h}{2\pi}$, where h is Planck's constant.