On Invariant Representation of High-Dimensional Functions: Spherical Shell Potentials

N. C. Nguyen

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Abstract

In this note, we introduce a systematic approach for constructing invariant high-dimensional functions. These functions are invariant under permutation, translation, and rotation of the reference frame. We obtain a new class of nonparametric potentials for molecular dynamics simulations by combining the invariant functions developed herein with regression methods. Although we consider molecular dynamics simulations, our approach may find applications in other areas of engineering and science.

1 The Curse of Dimensionality and Invariances

A molecular dynamics (MD) simulation produces a dynamical trajectory for a system composed of N particles by integrating Newton's equations of motion:

$$m_n \frac{d^2 \boldsymbol{r}_n}{dt^2} = \boldsymbol{f}_n = -\frac{\partial U(\boldsymbol{r}_1, \dots \boldsymbol{r}_N)}{\partial \boldsymbol{r}_n}, \tag{1}$$

where $U(\boldsymbol{r}_1, \dots \boldsymbol{r}_N)$ is the potential energy depending on the coordinates of the N particles, and m_n and $\boldsymbol{r}_n$ represent the mass and coordinates of the nth particle, respectively. Apart from the fact that the potential energy is a very high-dimensional function in $\mathbb{R}^{3N}$, it has a number of crucial invariant properties

- Permutation: Swapping two atoms of the same type does not change the potential energy, namely, $U(\boldsymbol{r}_1, \boldsymbol{r}_2, \dots, \boldsymbol{r}_N) = U(\boldsymbol{r}_2, \boldsymbol{r}_1, \dots, \boldsymbol{r}_N)$ if atom 1 and atom 2 are of the same type.

- Translation: Shifting the reference frame does not change the potential energy, namely, $U(\boldsymbol{r}_1 - \boldsymbol{r}, \dots, \boldsymbol{r}_N - \boldsymbol{r}) = U(\boldsymbol{r}_1, \dots, \boldsymbol{r}_N)$ for any $\boldsymbol{r} \in \mathbb{R}^3$.

- Rotation: Rotating the reference frame does not change the potential energy, namely, $U(\boldsymbol{R}(\alpha, \beta, \gamma)\boldsymbol{r}_1, \dots, \boldsymbol{R}(\alpha, \beta, \gamma)\boldsymbol{r}_N) = U(\boldsymbol{r}_1, \dots, \boldsymbol{r}_N)$, for any rotation matrix $\boldsymbol{R}(\alpha, \beta, \gamma)$, where α, β, γ are Euler angles.

In this note, we introduce a systematic approach for constructing a basis set of high-dimensional functions, $\{d_m(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)\}_{m=1}^{M}$, that are invariant under permutation of atoms of the same type, translation and rotation of the reference frame. These invariant high-dimensional functions will allow us to represent the potential energy in many different ways. For instance, we can express the potential energy as a linear combination of those functions:

$$U(\boldsymbol{r}_1, \ldots \boldsymbol{r}_N) = \sum_{m=1}^{M} a_m d_m(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N). \tag{2}$$

The coefficients a_m can be determined by fitting the potential energy representation (2) to the available data. More generally, we can perform linear regression, nonlinear regression, or neural network regression to construct a specific form of the potential energy using the above set of high-dimensional basis functions.

2 Permutation Invariance

To tackle the curse of dimensionality, we begin by posing a question: Given a one dimensional function $u(x)$ for $x \in \mathbb{R}$, how do we create two-dimensional functions? Naturally, both $f(x, y) = u(x)u(y)$ and $g(x, y) = u(x) + u(y)$ give us the answer to the above question. The product representation is not interesting, since it does not allow us to perform combinations such as this $\alpha u(x) + \beta u(y)$. Hence, we prefer the additive representation. The concept can be generalized to any dimensions so we have that $g(x_1, x_2, \ldots, x_N) = \sum_{i=1}^{N} u(x_i)$ is a function in $\mathbb{R}^N$. So, to create a $3N$-dimensional function from a 3-dimensional function $u(\boldsymbol{r})$, we may simply set

$$d(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) := \sum_{i=1}^{N} u(\boldsymbol{r}_i) \ .$$

We see that the function d is invariant to permutation since swapping $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ does not change the value of the function.

What kind of function $u(\boldsymbol{r})$ one can choose? Since the representation of the potential energy can not be settled with one function, we must actually look for function spaces. Hilbert spaces arise naturally in mathematics and physics, as infinite-dimensional function spaces for solutions of partial differential equations. Hilbert spaces that are suitable for our purpose are the spaces of square-integrable functions, namely, the Lebesgue spaces. Let us assume that the atoms reside in a bounded physical domain $\Omega \in \mathbb{R}^3$, that is, $\boldsymbol{r}_n \in \Omega$ for all $n \in [1, N]$. Then the Lebesgue space is defined as

$$L_2(\Omega) = \left\{ u \ : \ \int_{\Omega} |u(\boldsymbol{r})|^2 d\boldsymbol{r} < \infty \right\}.$$

Let us assume that we are able to construct a set of basic functions $\{u_m\}$ such that

$$L_2(\Omega) = \text{span}\{u_m, \ m = 1, \ldots, \infty\}.$$

We can use them to generate high-dimensional functions as follows

$$d_m(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) := \sum_{i=1}^{N} u_m(\boldsymbol{r}_i), \qquad m = 1, \ldots, \infty \ .$$

However, these high-dimensional functions are not invariant under translation and rotation of the reference frame. We address translation invariance in Section 3 and rotation invariance in Section 4. In the remainder, we use $\boldsymbol{r}^N$ in place of $(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)$ to simplify the notation.

3 Translation Invariance

To have the property of translation invariance, we may conveniently choose an atom n and associate it with a physical domain Ω_n such that $\boldsymbol{r}_i - \boldsymbol{r}_n \in \Omega_n$ for all atoms $i \in [1, N]$. We then introduce

$$c_{nm}(\boldsymbol{r}_1 - \boldsymbol{r}_n, \ldots, \boldsymbol{r}_N - \boldsymbol{r}_n) := \sum_{i=1}^{N} u_{nm}(\boldsymbol{r}_i - \boldsymbol{r}_n), \qquad m = 1, \ldots, \infty \ , \tag{3}$$

where $\{u_{nm}(\boldsymbol{r})\}_{m=1}^{\infty} \in L^2(\Omega_n)$ is a basic set for the Lebesgue space $L^2(\Omega_n)$. Since $(\boldsymbol{r}_i - \boldsymbol{r}) - (\boldsymbol{r}_n - \boldsymbol{r}) = \boldsymbol{r}_i - \boldsymbol{r}_n$ for any $\boldsymbol{r} \in \mathbb{R}^3$, shifting the coordinates of all atoms does not change c_{nm}. Hence, the functions c_{nm} are invariant with respect to translation. To eliminate the arbitrary of choosing an atom n, we must apply the formula (3) to all atoms of the system. We can now introduce

$$d_m(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) = \sum_{n=1}^{N} c_{nm}(\boldsymbol{r}_1 - \boldsymbol{r}_n, \ldots, \boldsymbol{r}_N - \boldsymbol{r}_n) = \sum_{n=1}^{N} \sum_{i=1}^{N} u_{nm}(\boldsymbol{r}_i - \boldsymbol{r}_n). \tag{4}$$

The new functions d_m are invariant under translation of the reference frame. The translation invariance comes with the cost of creating N different basis sets and evaluating the double sum in (4) at $O(N^2)$ operation counts. Both issues can be remedied as follows.

To reduce the number of basis sets from N to 1, we select one fixed reference domain Ω_{ref} and map all of the domains $\Omega_n, 1, \ldots, N$ to the reference domain Ω_{ref}. Let us consider

$$\Omega_n = \{\boldsymbol{r} \in \mathbb{R}^3 \ : \ r_{\min} < |\boldsymbol{r} - \boldsymbol{r}_n| < r_{\max}\}, \qquad n = 1, \ldots, N$$

where $r_{\max}$ is a cutoff radius and $r_{\min} > 0$ is introduced as a means to ensure that two atoms can not occupy the same position, thereby avoiding singularities at $r = 0$ as we shall discuss later. Then all the domains Ω_n can be mapped to the following reference domain by a simple translation

$$\Omega_{\mathrm{ref}} = \{\boldsymbol{r} \in \mathbb{R}^3 \ : \ r_{\min} < |\boldsymbol{r}| < r_{\max}\}. \tag{5}$$

Because translating a domain does not change function spaces defined on it, we have that $L_2(\Omega_n) \equiv L_2(\Omega_{\mathrm{ref}})$ for all n. Let us assume that we are given a basis set $\{u_m\}$ such that

$$L_2(\Omega_{\mathrm{ref}}) = \mathrm{span}\{u_m, \ m = 1, \ldots, \infty\}. \tag{6}$$

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We introduce associated high-dimensional functions

$$d_m(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) = \sum_{n=1}^{N} \sum_{i}^{\boldsymbol{r}_i \in \Omega_n} u_m(\boldsymbol{r}_i - \boldsymbol{r}_n), \quad m = 1, \ldots, \infty. \tag{7}$$

Apart from reducing the number of basis sets from N to 1, the computational cost of evaluating the double sum in (7) should be considerably less than $O(N^2)$ if the number of neighbors within the cutoff distance $r_{\max}$ is significantly less than N.

The set of high-dimensional functions in (7) is introduced for systems in which all atoms are of the same type. To distinguish atoms of different types and characterize the interactions of atoms of different types, we introduce

$$d_m(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) = \sum_{n=1}^{N} \sum_{i}^{\boldsymbol{r}_i \in \Omega_n} w_{Z_n Z_i} u_m(\boldsymbol{r}_i - \boldsymbol{r}_n), \quad m = 1, \ldots, \infty, \tag{8}$$

where $w_{Z_n Z_i}$ are the dimensionless weights and $Z_i \in [1, n_{\text{type}}]$ is an integer number indicating the type of atom i. Here n_{type} is the number of atom types existing in the system. We set $w_{11} = 1$ to reduce the number of weights by 1. Hence, the total number of weights is $n_{\text{type}}(n_{\text{type}} + 1)/2 - 1$.

However, because the functions d_m are not invariant under rotation of the reference frame, they should not be used to represent the potential energy. Another challenge is to construct an appropriate basis set $\{u_m\}$. Ideally, this basis set allows us to capture various interactions among atoms including both bonded interactions (e.g., stretching, bending, torsion, and dihedral interactions) and non-bonded interactions (e.g., electrostatic and van der Waals interactions). Both issues are addressed in the next section.

4   Rotation Invariance

4.1   The construction of an appropriate basis set

Due to the introduction of the cutoff radius, we would like our basis functions $u_m(\boldsymbol{r})$ to be zero at $|\boldsymbol{r}| = r_{\max}$. This will guarantee a smooth decay to zero beyond the cutoff distance. Henceforth, we introduce the following Lebesgue space of square-integrable functions

$$L_2^0(\Omega_{\text{ref}}) = \left\{ u \; : \; \int_\Omega |u(\boldsymbol{r})|^2 d\boldsymbol{r} < \infty \text{ and } u(\boldsymbol{r}) = 0 \text{ for } |\boldsymbol{r}| = r_{\max} \right\}. \tag{9}$$

In our method, the atomic interactions beyond the cutoff distance are automatically filtered through basis functions that satisfy the homogeneous Dirichlet condition. In contrast, most empirical and machine learning potentials screen the atomic interactions by introducing a cutoff function $f_{\max}(|\boldsymbol{r}|, r_{\max})$ that decreases smoothly from 1 at the origin to 0 at the cutoff distance.

We might attempt to look for basis functions that form a complete set of orthonormal functions and thus form an orthonormal basis of the Lebesgue space $L_2^0(\Omega_{\text{ref}})$. It turns

out that the complete orthonormal basis set may contain many basis functions that do not capture the atomic interactions. Basis functions that do not capture the physics of the underlying system are redundant and should not be removed. It means that we want a basis set that has sufficient basis functions to capture various atomic interactions. To this end, we consider the eigenvalue problem

$$\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial u}{\partial r} + \frac{1}{r^2}\left(\frac{1}{\sin^2\theta}\frac{\partial^2 u}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial u}{\partial\theta}\right) = -\lambda u, \quad \text{in } \Omega_{\text{ref}}, \tag{10}$$

with the boundary condition $u(\boldsymbol{r}) = 0$ for $|\boldsymbol{r}| = r_{\max}$. It is well known that the general solution of the problem (10) is given by

$$u(\boldsymbol{r}) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l}(\alpha_{lm}j_l(\sqrt{\lambda}r) + \beta_{lm}y_l(\sqrt{\lambda}r))Y_{lm}(\theta,\phi). \tag{11}$$

Here the spherical harmonics of degree l and order m are given by

$$Y_{lm}(\theta,\phi) = \sqrt{\frac{(2l+1)}{4\pi}\frac{(l-m)!}{(l+m)!}}P_{lm}(\cos(\theta))e^{im\phi}, \qquad l \geq 0, m = -l,\ldots,l \tag{12}$$

with P_{lm} being the associated Legendre polynomials. The spherical harmonics form a complete set of orthogonal functions and thus an orthonormal basis of the space of square-integrable functions $L_2(S^2)$. Figure 1 shows Y_{lm} for different values of (l,m). It is well known that the spherical harmonics yield electron orbitals of hydrogen atoms. Indeed, they represent the different quantized configurations of atomic orbitals. In particular, the angular momentum quantum number l represents the orbital shape, while the magnetic quantum number m represents the orbital orientation.

The functions j_l and y_l in (11) are known as the spherical Bessel functions

$$j_l(r) = (-r)^l\left(\frac{1}{x}\frac{d}{dr}\right)^l\frac{\sin r}{r}, \qquad y_l(x) = (-r)^l\left(\frac{1}{r}\frac{d}{dr}\right)^l\frac{\cos r}{r}, \quad l \geq 0. \tag{13}$$

Note that $j_l(r)$ is bounded as $r \to 0$ since we have $j_0(0) = 1$ and $j_l(0) = 0$ for $l \geq 1$. In contrast, $y_l(r)$ is unbounded as $r \to 0$. It follows from quantum mechanical theory that the potential energy increases rapidly and becomes unbounded when the distance between two atoms approaches zero. This phenomenon is due to the repulsive interactions (Pauli repulsion) of two atoms at short distance. Indeed, the Lennard-Jones potential has a repulsive term which scales as $1/r^{12}$. As a result, we want our solution to be unbounded as $r \to 0$. By setting $\alpha_{lm} = 0$, we obtain

$$u(\boldsymbol{r}) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l}\beta_{lm}y_l(\sqrt{\lambda}r)Y_{lm}(\theta,\phi).$$

The boundary condition $u = 0$ on $\partial\Omega_{\text{ref}}$ gives us
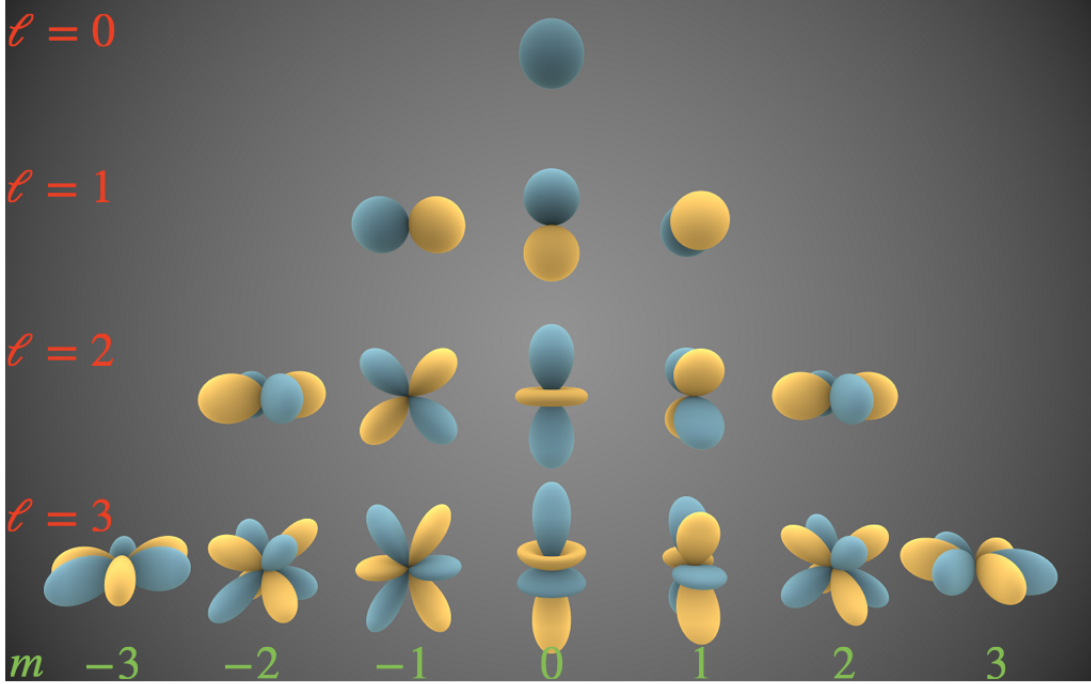
$$y_l(\sqrt{\lambda}r_{\max}) = 0.$$

Figure 1: Visual representations of the first few real spherical harmonics. Blue portions represent regions where the function is positive, and yellow portions represent where it is negative. The distance of the surface from the origin indicates the absolute value of $Y_\ell^m(\theta, \phi) Y_\ell^m(\theta, \phi)$ in angular direction (θ, ϕ). The image is taken from https://en.wikipedia.org/wiki/Spherical_harmonics.

Hence, the eigenvalues are those values of λ for which $\sqrt{\lambda} r_{\max} = \xi_{lk}$, where ξ_{lk} is the kth positive zero of y_k. Thus, the eigenvalues are given by

$$\lambda_{lk} = \left(\frac{\xi_{lk}}{r_{\max}} \right)^2. \tag{14}$$

As a result, the desired solution has the form

$$u(\boldsymbol{r}) = \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \gamma_{klm} y_l \left(\frac{\xi_{lk}}{r_{\max}} r \right) Y_{lm}(\theta, \phi). \tag{15}$$

Figure 2 shows $y_l \left(\frac{\xi_{lk}}{r_{\max}} r \right)$ for different values of (l, k). Notice that those functions smoothly go to zero at $r = r_{\max}$. We see that those functions are capable of capturing monopole electrostatic interaction terms $1/r$, attractive dispersive interaction terms $1/r^6$, and repulsive interaction terms $1/r^{12}$. A linear combination of those functions can capture a wide range of electrostatic interactions terms $1/r^n$ for $n \geq 1$ including charge-charge, charge-dipole, dipole-dipole, and quadrupole-quadrupole interactions.
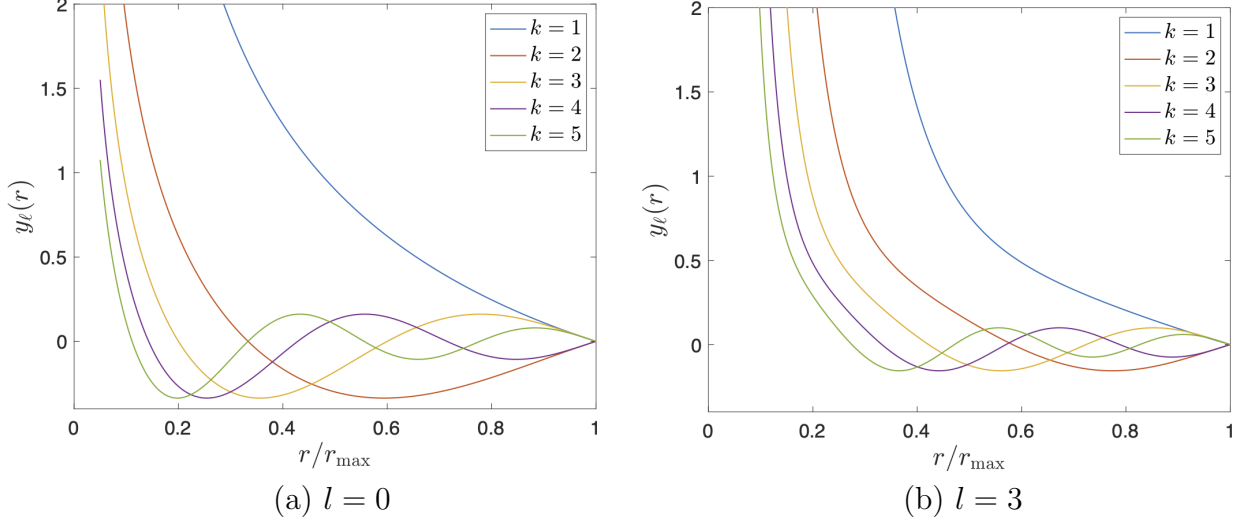
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Figure 2: Visual representations of the spherical Bessel functions $y_l\left(\frac{\xi_{lk}}{r_{\max}}r\right)$.

The spherical harmonics are orthonormal on the 2-sphere S^2, but the spherical Bessel functions are not orthonormal on the interval $[r_{\min}, r_{\max}]$. We orthogonalize the spherical Bessel functions to obtain orthonormal functions as follows

$$g_{lk}(r) = \sum_{l'}\sum_{k'} W_{lkl'k'}\ y_{l'}\left(\frac{\xi_{l'k'}}{r_{\max}}r\right)$$

where the matrix $\boldsymbol{W}$ is obtained from the matrix $\boldsymbol{S}$ as $\boldsymbol{W} = \boldsymbol{S}^{-1/2}$ with

$$S_{lkl'k'} = \int_{r_{\min}}^{r_{\max}} y_l\left(\frac{\xi_{lk}}{r_{\max}}r\right) y_{l'}\left(\frac{\xi_{l'k'}}{r_{\max}}r\right) r^2 dr \ .$$

Note that $g_{lk}(r)$ depends on both $r_{\min}$ and $r_{\max}$. Since the spherical Bessel functions are singular at $r = 0$, approaching that point as r^{-l-1}, many entries of the matrix $\boldsymbol{S}$ are infinite if we take $r_{\min} = 0$. For a fixed value $r_{\min} > 0$, all the entries of the matrix $\boldsymbol{S}$ are finite. Finally, we introduce the function space

$$W^0(\Omega_{\text{ref}}) = \text{span}\left\{u_{klm}(\boldsymbol{r}) = g_{lk}(r)Y_{lm}(\theta, \phi), \quad k \geq 1, l \geq 0, \text{and } m = -l, \ldots, l\right\},$$

which has an orthogonal property

$$\int_0^{2\pi}\int_0^\pi\int_{r_{\min}}^{r_{\max}} u_{klm}(\boldsymbol{r})u_{k'l'm'}(\boldsymbol{r})r^2\sin\theta dr d\theta d\phi = \delta_{kk'}\delta_{ll'}\delta_{mm'} \ .$$

In practice, we employ a subspace of $W^0(\Omega_{\text{ref}})$ defined as follows

$$W_M^0(\Omega_{\text{ref}}) = \text{span}\left\{u_{klm}(\boldsymbol{r}) = g_{lk}(r)Y_{lm}(\theta, \phi), \quad 1 \leq k \leq K, 0 \leq l \leq L, -l \leq m \leq l\right\}. \quad (16)$$

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This subspace has M basis functions with $M = K(L+1)^2$. It is obvious that $W_M^0(\Omega_{\mathrm{ref}}) \subset W^0(\Omega_{\mathrm{ref}}) \subset L_2^0(\Omega_{\mathrm{ref}})$.

As evident later, we will use the subspace W_M^0 to construct invariant high-dimensional functions. This subspace is established from the eigenfunctions of the Laplace operator in the spherical shell Ω_{ref}. The choice of the Laplace operator and the spherical shell is based on our prior knowledge of the atomic interactions as well as quantum theory of angular momentum discussed in the next section.

4.2   Spherical harmonics

Spherical harmonics are eigenfunctions of the Laplace-Beltrami operator on the 2-sphere (the surface of the 3D sphere). They represent the angular portion of a set of solutions to the Laplace's equation (10), while the spherical Bessel functions represent the radial portion. Since the spherical harmonics form a complete set of orthogonal functions and thus an orthonormal basis, any function defined on the 2-sphere can be written as a sum of spherical harmonics. Spherical harmonics are basis functions for irreducible representations of SO(3), the group of rotations in three dimensions, and thus play a central role in the SO(3) group. In particular, the spherical harmonics of degree l provide a basis set of functions for the irreducible representation of the group SO(3) of dimension $2l+1$. For a given degree l, let us define the subspace of functions

$$V_l = \mathrm{span}\{Y_{l,-l}, Y_{l,-l+1}, \ldots, Y_{l,l-1}, Y_{l,l}\}.$$

For any function $f \in V_l$, we have $\mathcal{R}(\alpha, \beta, \gamma)f \in V_l$, where $\mathcal{R}(\alpha, \beta, \gamma)$ is the rotation operator acting on a function described by the Euler angles (α, β, γ). Furthermore, the subspace V_l is irreducible in the sense that one can not find another subspace W_m of dimension $m < 2l+1$ such that $\mathcal{R}(\alpha, \beta, \gamma)f \in W_m$. In other words, the rotation of any function $f \in V_l$ can be represented *exactly* as follows

$$\mathcal{R}(\alpha, \beta, \gamma)f(\theta, \phi) \equiv f(\theta', \phi') = \sum_{m=-l}^{l} a_m(\alpha, \beta, \gamma), Y_{lm}(\theta, \phi), \tag{17}$$

where (θ', ϕ') are polar angles of the position vector $\boldsymbol{r}' = (\theta', \phi', r)$ obtained by rotating the vector $\boldsymbol{r} = (\theta, \phi, r)$ with the Euler angles (α, β, γ). Multiplying both sides of (17) by $\bar{Y}_{lm'}(\boldsymbol{r})$ (the bar symbol denotes the complex conjugate) and integrating it over the 2-sphere yields

$$a_m(\alpha, \beta, \gamma) = \int_0^{2\pi} \int_0^{\pi} \bar{Y}_{lm'}(\theta, \phi)\mathcal{R}(\alpha, \beta, \gamma)f(\theta, \phi)\sin\theta d\theta d\phi, \quad m = -l, \ldots, l.$$

The irreducible representation of the SO(3) group from subspaces formed by spherical harmonics functions allows us to establish some important results as discussed next.

It follows from the above discussion that an arbitrary rotation of a spherical harmonic function Y_{lm} transforms it into a linear combination of spherical harmonics with the same l

index

$$\mathcal{R}(\alpha, \beta, \gamma) Y_{lm}(\theta, \phi) = \sum_{m'=-l}^{l} Y_{lm'}(\theta, \phi) D_{mm'}^{l}(\alpha, \beta, \gamma), \qquad (18)$$

where

$$D_{mm'}^{l}(\alpha, \beta, \gamma) = \int_{0}^{2\pi} \int_{0}^{\pi} \bar{Y}_{lm'}(\theta, \phi) \mathcal{R}(\alpha, \beta, \gamma) Y_{lm}(\theta, \phi) \sin \theta d\theta d\phi.$$

The $\boldsymbol{D}^{l}(\boldsymbol{r}, \omega)$ matrices of size $(2l+1) \times (2l+1)$ are known as the Wigner matrices. It follows from quantum theory of angular momentum that the Wigner matrices are eigenfunctions of three operators: $\hat{\mathcal{J}}_{z} = -i\frac{\partial}{\partial \alpha}$, $\hat{\mathcal{J}}_{z'} = -i\frac{\partial}{\partial \gamma}$, and $\mathcal{J}^{2} = -\frac{1}{\sin^{2}\beta} \left(\frac{\partial^{2}}{\partial \alpha^{2}} + \frac{\partial^{2}}{\partial \gamma^{2}} - 2\cos\beta \frac{\partial^{2}}{\partial \alpha \partial \gamma} \right) - \frac{\partial^{2}}{\partial \beta^{2}} - \cot\beta \frac{\partial}{\partial \beta}$. Hence, the Wigner matrices are orthogonal and unitary:

$$\left(\boldsymbol{D}^{l}(\alpha, \beta, \gamma) \right)^{\mathrm{H}} \boldsymbol{D}^{l}(\alpha, \beta, \gamma) = \boldsymbol{I}, \qquad l \geq 0, \qquad (19)$$

where the superscript H denotes the Hermitian conjugate. The Wigner matrices $\boldsymbol{D}^{l}(\alpha, \beta, \gamma)$ constitute the irreducible tensors of rank l for both the SO(3) group and the SU(2) group.

4.3   Rotational invariants

We use the theory of angular momentum described earlier to construct rotationally invariant functions. To keep our presentation clear, we describe our approach for basis functions which are the products of spherical harmonics and Bessel functions. In the next section, we use the results derived here to obtain a new class of nonparametric potentials. We begin with considering the following high-dimensional functions

$$a_{lm}(\boldsymbol{r}^{N}) = \sum_{i}^{N} y_{l}(r_{i}) Y_{lm}(\theta_{i}, \phi_{i}), \qquad l \geq 0, m = -l, \ldots, l,$$

which transform under rotation as

$$\begin{aligned}
\mathcal{R}(\alpha, \beta, \gamma) a_{lm}(\boldsymbol{r}^{N}) &= \sum_{i}^{N} y_{l}(r_{i}) \mathcal{R}(\alpha, \beta, \gamma) Y_{lm}(\theta_{i}, \phi_{i}) \\
&= \sum_{i}^{N} y_{l}(r_{i}) \sum_{m'=-l}^{l} D_{mm'}^{l}(\alpha, \beta, \gamma) Y_{lm'}(\theta_{i}, \phi_{i}) \\
&= \sum_{i}^{N} \sum_{m'=-l}^{l} D_{mm'}^{l}(\alpha, \beta, \gamma) y_{l}(r_{i}) Y_{lm'}(\theta_{i}, \phi_{i}) \\
&= \sum_{m'=-l}^{l} D_{mm'}^{l}(\alpha, \beta, \gamma) a_{lm'}(\boldsymbol{r}^{N}).
\end{aligned}$$

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This equation can be written in matrix form as

$$\mathcal{R}(\alpha, \beta, \gamma)\boldsymbol{a}_l(\boldsymbol{r}^N) = \boldsymbol{D}^l(\alpha, \beta, \gamma)\boldsymbol{a}_l(\boldsymbol{r}^N).$$

Because $\boldsymbol{a}_l(\boldsymbol{r}^N)$ change their values when we apply the rotation operator to them, they are not invariant under the rotation of the reference frame. Let us consider the rotation of their inner products:

$$
\begin{aligned}
\mathcal{R}(\alpha, \beta, \gamma)\big((\boldsymbol{a}_l(\boldsymbol{r}^N))^{\mathrm{H}}\boldsymbol{a}_l(\boldsymbol{r}^N)\big) &= \big(\mathcal{R}(\alpha, \beta, \gamma)\boldsymbol{a}_l(\boldsymbol{r}^N)\big)^{\mathrm{H}}\big(\mathcal{R}(\alpha, \beta, \gamma)\boldsymbol{a}_l(\boldsymbol{r}^N)\big) \\
&= \big(\boldsymbol{D}^l(\alpha, \beta, \gamma)\boldsymbol{a}_l(\boldsymbol{r}^N)\big)^{\mathrm{H}}\big(\boldsymbol{D}^l(\alpha, \beta, \gamma)\boldsymbol{a}_l(\boldsymbol{r}^N)\big) \\
&= \big(\boldsymbol{a}_l(\boldsymbol{r}^N)\big)^{\mathrm{H}}\big(\boldsymbol{D}^l(\alpha, \beta, \gamma)\big)^{\mathrm{H}}\big(\boldsymbol{D}^l(\alpha, \beta, \gamma)\big)\boldsymbol{a}_l(\boldsymbol{r}^N) \\
&= \big(\boldsymbol{a}_l(\boldsymbol{r}^N)\big)^{\mathrm{H}}\boldsymbol{a}_l(\boldsymbol{r}^N),
\end{aligned}
$$

which remain the same value when the rotation operator acts upon them. Therefore, the following quantities called the power spectrum

$$p_l(\boldsymbol{r}^N) = \big(\boldsymbol{a}_l(\boldsymbol{r}^N)\big)^{\mathrm{H}}\boldsymbol{a}_l(\boldsymbol{r}^N), \qquad l \geq 0, \tag{20}$$

are invariant to the rotation of the reference frame. Notice that we make use of (18) and (19) to obtain the power spectrum (20).

The concept of the power spectrum can be generalized to obtain a larger set of rotational invariants by coupling higher-order angular momentum. To this end, we consider the tensor product $\boldsymbol{a}_{l_1}(\boldsymbol{r}^N) \otimes \boldsymbol{a}_{l_2}(\boldsymbol{r}^N))$, which transforms under a rotation as

$$
\begin{aligned}
\mathcal{R}(\alpha, \beta, \gamma)\big(\boldsymbol{a}_{l_1}(\boldsymbol{r}^N) \otimes \boldsymbol{a}_{l_2}(\boldsymbol{r}^N)\big) &= \big(\mathcal{R}(\alpha, \beta, \gamma)\boldsymbol{a}_{l_1}(\boldsymbol{r}^N)\big) \otimes \big(\mathcal{R}(\alpha, \beta, \gamma)\boldsymbol{a}_{l_2}(\boldsymbol{r}^N)\big) \\
&= \big(\boldsymbol{D}^{l_1}(\alpha, \beta, \gamma)\boldsymbol{a}_{l_1}(\boldsymbol{r}^N)\big) \otimes \big(\boldsymbol{D}^{l_2}(\alpha, \beta, \gamma)\boldsymbol{a}_{l_2}(\boldsymbol{r}^N)\big) \tag{21} \\
&= \big(\boldsymbol{D}^{l_1}(\alpha, \beta, \gamma) \otimes \boldsymbol{D}^{l_2}(\alpha, \beta, \gamma)\big)\big(\boldsymbol{a}_{l_1}(\boldsymbol{r}^N) \otimes \boldsymbol{a}_{l_2}(\boldsymbol{r}^N)\big).
\end{aligned}
$$

It follows from the representation theory of compact groups that the tensor product of two Wigner matrices can be decomposed into the product of three unitary matrices as

$$\boldsymbol{D}^{l_1}(\alpha, \beta, \gamma) \otimes \boldsymbol{D}^{l_2}(\alpha, \beta, \gamma) = (\boldsymbol{C}^{l_1 l_2})^{\mathrm{H}}\left(\bigoplus_{l=|l_1-l_2|}^{l_1+l_2} \boldsymbol{D}^l(\alpha, \beta, \gamma)\right)(\boldsymbol{C}^{l_1 l_2}), \tag{22}$$

where

$$\bigoplus_{l=|l_1-l_2|}^{l_1+l_2} \boldsymbol{D}^l(\alpha, \beta, \gamma) \equiv \begin{bmatrix} \boldsymbol{D}^{|l_1-l_2|} & & & \\ & \boldsymbol{D}^{|l_1-l_2|+1} & & \\ & & \ddots & \\ & & & \boldsymbol{D}^{l_1+l_2} \end{bmatrix}.$$

Here $\boldsymbol{C}^{l_1 l_2}$ are unitary matrices formed by the Clebsch-Gordan coefficients $C^{l_1 l_2 l}_{m_1 m_2 m}$. It follows from (21) and (22) that

$$\mathcal{R}(\alpha, \beta, \gamma)\Big(\boldsymbol{C}^{l_1 l_2}\big(\boldsymbol{a}_{l_1}(\boldsymbol{r}^N) \otimes \boldsymbol{a}_{l_2}(\boldsymbol{r}^N)\big)\Big) = \left(\bigoplus_{l=|l_1-l_2|}^{l_1+l_2} \boldsymbol{D}^l(\alpha, \beta, \gamma)\right)\boldsymbol{C}^{l_1 l_2}\big(\boldsymbol{a}_{l_1}(\boldsymbol{r}^N) \otimes \boldsymbol{a}_{l_2}(\boldsymbol{r}^N)\big).$$

By introducing a set of vectors $\boldsymbol{c}_{ll_1l_2}(\boldsymbol{r}^N)$ with entries

$$c_{ll_1l_2m}(\boldsymbol{r}^N) = \sum_{m_1=-l_1}^{l_1} \sum_{m_2=-l_2}^{l_2} C_{m_1m_2m}^{l_1l_2l} a_{l_1m_1}(\boldsymbol{r}^N) a_{l_2m_2}(\boldsymbol{r}^N), \qquad m = -l, \ldots, l$$

we can write

$$\boldsymbol{C}^{l_1l_2}\big(\boldsymbol{a}_{l_1}(\boldsymbol{r}^N) \otimes \boldsymbol{a}_{l_2}(\boldsymbol{r}^N)\big) = \bigoplus_{l=|l_1-l_2|}^{l_1+l_2} \boldsymbol{c}_{ll_1l_2}.$$

Hence, we obtain

$$\mathcal{R}(\alpha,\beta,\gamma)\left(\bigoplus_{l=|l_1-l_2|}^{l_1+l_2} \boldsymbol{c}_{ll_1l_2}\right) = \left(\bigoplus_{l=|l_1-l_2|}^{l_1+l_2} \boldsymbol{D}^l(\alpha,\beta,\gamma)\right)\bigoplus_{l=|l_1-l_2|}^{l_1+l_2} (\boldsymbol{c}_{ll_1l_2})$$

which is equivalent to

$$\mathcal{R}(\alpha,\beta,\gamma)\boldsymbol{c}_{ll_1l_2}(\boldsymbol{r}^N) = \boldsymbol{D}^l(\alpha,\beta,\gamma)\boldsymbol{c}_{ll_1l_2}(\boldsymbol{r}^N).$$

By the same argument as for the power spectrum, the following quantities called the bispectrum

$$
\begin{aligned}
b_{ll_1l_2}(\boldsymbol{r}^N) &= (\boldsymbol{a}_l(\boldsymbol{r}^N))^{\mathrm{H}} \boldsymbol{c}_{ll_1l_2}(\boldsymbol{r}^N) \\
&= \sum_{m=-l_1}^{l} \sum_{m_1=-l_1}^{l_1} \sum_{m_2=-l_2}^{l_2} \bar{a}_{lm}(\boldsymbol{r}^N) C_{m_1m_2m}^{l_1l_2l} a_{l_1m_1}(\boldsymbol{r}^N) a_{l_2m_2}(\boldsymbol{r}^N),
\end{aligned}
\tag{23}
$$

are invariant under the rotation of the reference frame.

5   Spherical Shell Potentials

In this section, we use the theory of invariant functions developed herein to construct a new class of nonparametric interactomic potentials. The building block of the proposed approach is the set of appropriately selected eigenfunctions of the Laplacian operator on a spherical shell. Hence we call this approach the spherical shell potentials.

5.1   Spherical shell potentials based on the power spectrum

Based on the theory of invariant functions described earlier, we introduce the following functions

$$a_{nklm}(\boldsymbol{r}^N) := \sum_i^{\boldsymbol{r}_i \in \Omega_n} w_{Z_n Z_i} u_{klm}(\boldsymbol{r}_i - \boldsymbol{r}_n), \qquad m = -l, \ldots, l. \tag{24}$$

Here u_{mlk} are the basic functions of the subspace $W_M^0(\Omega_{\text{ref}})$ defined in (16). These functions allow us to construct a set of invariant functions as follows:

$$p_{nkk'l}(\boldsymbol{r}^N) = \left(\boldsymbol{a}_{nkl}(\boldsymbol{r}^N)\right)^{\text{H}} \boldsymbol{a}_{nk'l}(\boldsymbol{r}^N), \qquad 1 \le n \le N, 1 \le k \le K, 0 \le l \le L, k' \ge k, \quad (25)$$

where $\boldsymbol{a}_{nkl}(\boldsymbol{r}^N)$ and $\boldsymbol{a}_{nk'l}(\boldsymbol{r}^N)$ are vectors of dimension $2l+1$ from (24). Although they are invariant with respect to permutation, translation, and rotation, the number of such functions can be too large to allow for an efficient construction of interatomic potentials. To reduce the number of functions, we perform a weighted sum of $p_{nkk'l}(\boldsymbol{r}^N)$ over all atoms of the same type to obtain the following functions

$$d_{jkk'l}(\boldsymbol{r}^N) = \sum_n^{Z_n=j} p_{nkk'l}(\boldsymbol{r}^N), \qquad 1 \le j \le n_{\text{type}}, 1 \le k \le K, 0 \le l \le L, k' \ge k, \quad (26)$$

where the sum is performed for all atoms of type j. We recall that $Z_n \in [1, n_{\text{type}}]$ is an integer number indicating the type of atom n, where n_{type} is the number of atom types.

For simplicity, we consider linear regression to construct the potential energy. Hence we define the potential energy as

$$U(\boldsymbol{r}^N) = \sum_{j=1}^{n_{\text{type}}} \sum_{k=1}^{K} \sum_{k' \ge k}^{K} \sum_{l=0}^{L} c_{jkk'l} d_{jkk'l}(\boldsymbol{r}^N) \equiv \left(\boldsymbol{d}(\boldsymbol{r}^N)\right)^T \boldsymbol{c} . \quad (27)$$

The coefficient vector $\boldsymbol{c}$ can be determined by fitting the potential energy representation (27) to the available data. Let a training set of n_{train} atomic configurations be $\boldsymbol{X}_{\text{train}} = \{\boldsymbol{r}_{\text{train}}^{N_q}, 1 \le q \le n_{\text{train}}\}$, where $\boldsymbol{r}_{\text{train}}^{N_q}$ consists of the coordinates of N_q atoms associated with configuration q. Let E^q and $\boldsymbol{f}^q$ be the reference energy and forces, which are obtained from quantum mechanical calculations for each configuration q. We form an overdetermined system of linear equations

$$\left(\boldsymbol{d}(\boldsymbol{r}_{\text{train}}^{N_q})\right)^T \boldsymbol{c} = E^q,$$
$$\frac{\partial}{\partial \boldsymbol{r}_j^{N_q}} \left(\boldsymbol{d}(\boldsymbol{r}_{\text{train}}^{N_q})\right)^T \boldsymbol{c} = \boldsymbol{f}_j^q, \qquad j = 1, \ldots, N_q, \quad (28)$$

for $q = 1, \ldots, n_{\text{train}}$. We rewrite this system in matrix form as $\boldsymbol{D}\boldsymbol{c} = \boldsymbol{e}$. The optimal solution $\boldsymbol{c}^*$ for this set of equations is

$$\boldsymbol{c}^* = \arg\min \|\boldsymbol{D}\boldsymbol{c} - \boldsymbol{e}\|. \quad (29)$$

We extend the linear regression method by performing weighted least squares to weight certain configurations more than others as follows

$$\boldsymbol{c}^* = \arg\min \|\boldsymbol{w} \odot (\boldsymbol{D}\boldsymbol{c} - \boldsymbol{e})\|, \quad (30)$$

where $\odot$ is used to denote element by element multiplication by the weight vector. Here the weigh vector $\boldsymbol{w}$ is assembled from the configuration weights $w_n, 1 \le n \le n_{\text{train}}$. In this

way, we are able to specify weights per configuration type (e.g. BCC crystals, liquids, etc.) and per number of atoms in each configuration (configuration with a large number of atoms should carry larger weights than a configuration with a small number of atoms.)

An alternative approach is to pursue sparse optimization method:

$$\min \|\boldsymbol{c}\|_p \quad \text{subject to} \quad \|\boldsymbol{D}\boldsymbol{c} - \boldsymbol{e}\| \leq \epsilon, \tag{31}$$

where p is either 0 or 1, and ϵ is a given accuracy threshold. Note that if there exists no $\boldsymbol{c} \in \mathbb{R}^{K^2(L+1)}$ that satisfies the constraint $\|\boldsymbol{D}\boldsymbol{c} - \boldsymbol{e}\| \leq \epsilon$, then we need to increase both L and K until we can find feasible solutions.

5.2 Spherical shell potentials based on the bispectrum

We begin by computing the bispectrum components as

$$b_{nkk'll_1l_2}(\boldsymbol{r}^N) = \sum_{m=-l_1}^{l} \sum_{m_1=-l_1}^{l_1} \sum_{m_2=-l_2}^{l_2} \bar{a}_{nklm}(\boldsymbol{r}^N) C_{m_1m_2m}^{l_1l_2l} a_{nk'l_1m_1}(\boldsymbol{r}^N) a_{nk'l_2m_2}(\boldsymbol{r}^N), \tag{32}$$

where the functions $a_{nklm}(\boldsymbol{r}^N)$ are defined in (24). The bispectrum components are invariant with respect to permutation of atoms of the same type, translation and rotation of the reference frame. Therefore, the following functions

$$d_{jkk'll_1l_2}(\boldsymbol{r}^N) = \sum_{n}^{Z_n=j} b_{nkk'll_1l_2}(\boldsymbol{r}^N), \quad 1 \leq j \leq n_{\text{type}}, 1 \leq k \leq K, 0 \leq l_1, l_2, l \leq L, k' \geq k, \tag{33}$$

also have the same invariant properties. The number of functions for the bispectrum is $n_{\text{type}}K(K+1)(L+1)^3/2$, which is significantly higher than that for the power spectrum. However, due to the symmetry properties of the Clebsch–Gordan coefficients and the spherical harmonic functions, we can reduce the number of functions substantially by removing redundant bispectrum components.

6 Further Extensions

In constructing nonparametric potentials, we choose our basis set to consist of eigenfunctions of the Laplacian operator on a spherical shell. Our choice is motivated by the fact that these eigenfunctions are not only analytical but also able to capture the main characteristics of local atomic environment such as electron orbitals, electrostatic interactions, and Van der Waals interactions. It is crucial to note that these eigenfunctions are independent of the underlying molecular dynamics system. Hence, the basis set can be applied to any MD simulations. As pointed below, these eigenfunctions are nothing but the wave functions of the Hamiltonian operator for a single particle subject to an appropriate potential function. This allows us to extend our approach by introducing different potential functions.
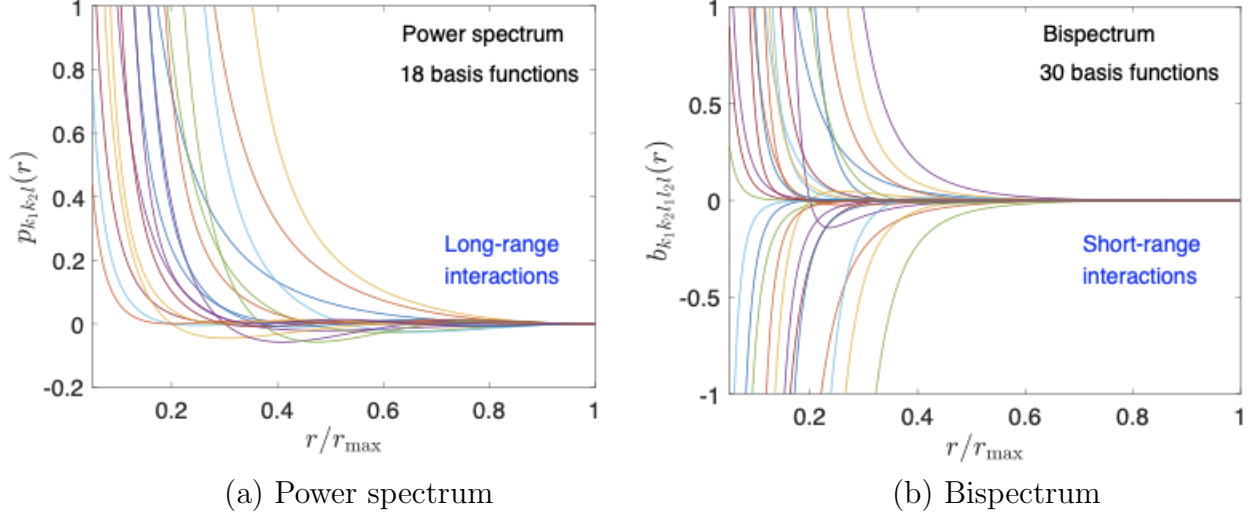
(a) Power spectrum	(b) Bispectrum

Figure 3: Radial basis functions of the power spectrum and bispectrum components.

To extend our method, we consider the Schrödinger equation for the wave function of a single particle subject to a potential function $V(\boldsymbol{r})$:

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r})\right]\psi = \lambda\psi, \qquad \text{in } \mathbb{R}^3, \tag{34}$$

where $\hbar$ is the reduced Planck constant and m is the mass of the particle. In the case of $V(\boldsymbol{r}) = 0$ (i.e. a free particle), the Schrödinger equation becomes the Laplacian eigenvalue problem. For the case in which

$$V(\boldsymbol{r}) = \begin{cases} 0, & |\boldsymbol{r}| \leq r_{\max} \\ \infty, & |\boldsymbol{r}| > r_{\max}, \end{cases} \tag{35}$$

the Schrödinger equation becomes

$$\nabla^2\psi = \lambda\psi, \qquad \text{in } \mathcal{B}^3_{r_{\max}}, \tag{36}$$

with the boundary condition $\psi(\boldsymbol{r}) = 0$ for $|\boldsymbol{r}| = r_{\max}$, where $\mathcal{B}^3_{r_{\max}}$ is a 3D ball of radius $r_{\max}$. Note that the eigenvalue probblem (36) is the same as the one in (10) when $r_{\min} = 0$. Other interesting potential functions include $V(\boldsymbol{r}) \sim r^2$ for the isotropic harmonic oscillator and $V(\boldsymbol{r}) \sim 1/r$ for the hydrogen-like atoms.