Non-Hermitian Quantum Mechanics Fundamentals & Lennard-Jones Potential

Larry Lee,[1] **Preet Sharma**[1][2]

[1] *Texas Academy of Mathematics & Science,*
Material Science & Engineering Track,
University of North Texas

[2] *Department of Chemistry & Physics,*
Midwestern State University

E-mail: `larrylee@my.unt.edu`, `preet.sharma@msutexas.edu`

Abstract:
Non-Hermitian quantum mechanics is a fairly new field and has been of great interests to theorists and experimentalists alike. In this study we have shown the basics of Non-Hermitian quantum mechanics and have put forward a scenario in which Non-Hermitian quantum mechanics can be applied to the well known Lennard-Jones potential. We have not shown explicitly what the results would be but when we apply Lennard-Jones potential to the Non-Hermitian scenario, but we have given one idea as to how it can play a part. This idea is also our continuing research.

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[1] Corresponding author.

1 Introduction: The Lennard-Jones Potential

The Lennard-Jones potential is a good approximation for an interatomic potential which is used in physics, chemistry and biology [1]. The general form of the Lennard-Jones potential follows from the following:

$$u(r) = \alpha r^{-n} - \beta r^{-m} \tag{1.1}$$

Where u is the pair potential, r is the interatomic distnace, and α, β, n, m are adjustable parameters [2] [3].

In the specific case of Lennard-Jones potential, the potential becomes:

$$u(r) = \alpha r^{-12} - \beta r^{-6} \tag{1.2}$$

This has two parts. The term with $\frac{1}{r^6}$ is the attraction part and the term with $\frac{1}{r^12}$ is the repulsive part. We can see clearly that it is a very short range potential and the is not felt at large distances. We do not wish to to too deep into the basics of Lennard-Jones potential. This section gives a brief description only.

2 Spherical Harmonics & Angular Momentum

2.0.1 Spherical Harmonics

Spherical harmonics play an important part in the description of the H-atom because they represent the solutions to the angular part of the wave function. The wave-function of the H-atom is given as [4–6]

$$\Psi_{nlm}(r, \theta, \phi) = R_{n,l}(r) Y_{lm}(\theta, \phi) \tag{2.1}$$

where the $Y_{lm}(\theta, \phi)$ are known as spherical harmonic functions given by

$$Y_{lm}(\theta, \phi) = (-1)^m \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} P_{lm}(\cos\theta) e^{(im\phi)} \tag{2.2}$$

for $m \geq 0$, and

$$Y_{l,-m}(\theta, \phi) = Y^*_{lm}(\theta, \phi) \tag{2.3}$$

for $m < 0$.

$P_{lm}(\cos\theta)$ are the associated Legendre polynomials given by,

$$P_{lm}(x) = (-1)^m \sqrt{(1-x^2)^m} \, \frac{d^m}{dx^m} P_l(x) \tag{2.4}$$

where $P_l(x)$ are Legendre polynomials. These polynomials can be generated using

$$P_l(x) = \frac{(-1)^l}{2^l l!} \frac{d^l}{dx^l} (1-x^2)^l \tag{2.5}$$

where $R_{n,l}(r)$ is the Radial part of the H-atom wave-function and is given by

$$R_{n,l}(r) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}}\; e^{-r/3a_0} L^{2l+1}_{n-l-1}\left(\frac{2r}{na_0}\right) \tag{2.6}$$

where $L^{2l+1}_{n-l-1}\left(\frac{2r}{na_0}\right)$ and is known as the associated Laguerre polynomials given by

$$L^{2l+1}_{n-l-1}(s) = \sum_{q=0}^{n-l-1} (-1)^q \; \frac{(n+l)!}{(n-l-q-1)!(q+2l+1)!} \; s^q \tag{2.7}$$

or, more generally as

$$L^{j}_{p}(s) = \sum_{q=0}^{p} (-1)^q \; \frac{(p+j)!}{(p-q)!(j+q)!q!} \; s^q \tag{2.8}$$

The spherical harmonics in eqn.(2.2) satisfy the orthonormality relations

$$\langle Y_{l',m'}(\theta,\phi)|Y_{lm}(\theta,\phi)\rangle = \int d\Omega \; Y_{l',m'}(\theta,\phi)Y_{lm}(\theta,\phi) = \delta_{m,m'} \; \delta_{l,l'} \tag{2.9}$$

where δ_{ab} is the Kronecker delta function.
The spherical harmonic functions form an orthonormal basis and hence, any function $f(\theta,\phi)$ can be written as

$$f(\theta,\phi) = \sum_{l\geq 0} \sum_{m=-l}^{l} C_{lm} Y_{lm}(\theta,\phi) \tag{2.10}$$

where the coefficients C_{lm} are

$$C_{lm} = \int d\Omega \; Y^*_{lm}(\theta,\phi) f(\theta,\phi) \tag{2.11}$$

Substituting C_{lm} in eqn.(2.10) and changing variables $u' = cos\theta'$ and $u = cos\theta$ results in

$$f(\theta,\phi) = \int_0^{2\pi} d\phi \int_{-1}^{1} du' f(u',\theta') \Big(\sum_{l\geq 0} \sum_{m=-l}^{l} Y^*_{lm}(u',\phi') Y_{lm}(u,\phi) \Big) \tag{2.12}$$

where the completeness relation for the spherical harmonics is given as

$$\sum_{l\geq 0} \sum_{m=-l}^{l} Y^*_{lm}(\theta',\phi') Y_{lm}(\theta,\phi) = \delta(\theta-\theta') \; \delta(cos\theta - cos\theta') \tag{2.13}$$

2.0.2 Angular Momentum

The angular momentum operators in the Hermitian space are given by,

$L_x = -i(y\partial_z - z\partial_y)$, $L_y = -i(z\partial_x - x\partial_z)$, $L_z = -i(x\partial_y - y\partial_x)$

and the angular momentum algebra is

$[L_x, L_y] = iL_z,\ [L_z, L_x] = iL_y,\ [L_y, L_z] = iL_x$ and $L_x^2 + L_y^2 + L_z^2 = L^2$

also, $[L^2, L_x] = [L^2, L_y] = [L^2, L_z] = 0$

The eigenvalue equation is given by

$$L^2 Y_{lm}(\theta, \phi) = l(l+1) Y_{lm}(\theta, \phi) \tag{2.14}$$

where $l = 0, 1, 2....$

3 $\mathcal{PT}$ Symmetric Spherical Harmonics & Angular Momentum

This section is a brief review of $\mathcal{PT}$ symmetry and the application to spherical harmonics and angular momentum [6, 7].

3.0.1 $\mathcal{PT}$ Symmetry Basics

In $\mathcal{PT}$ symmetry, $\mathcal{P}$ stands for the parity operator and $\mathcal{T}$ stands for the time reversal operator. When the parity operator is applied to a function it results in
$\mathcal{P}f(x, y, z) = f(-x, -y, -z)$
and the time reversal operator is defined when $t \to -t$ or $i \to -i$. So when the operator is applied $\mathcal{PT}$ the result is

$$\mathcal{PT}[f(\overrightarrow{x})] = f^*(-\overrightarrow{x})$$

In spherical harmonics the parity operator transforms as $(r, \theta, \phi) \to (r, \pi - \theta, \phi + \pi)$, so

$$\mathcal{PT}[f(r, \theta, \phi)] = f^*(r, \pi - \theta, \phi + \pi)$$

and with two functions $f \& g$

$$\langle f|g\rangle = \int d\overrightarrow{x}[\mathcal{PT}f(x)]g(x) \tag{3.1}$$

3.0.2 $\mathcal{PT}$ Symmetric Spherical Harmonics

Under the parity operator the spherical harmonics transform as

$$\mathcal{P}[Y_{lm}(\theta, \phi)] = Y_{lm}(\pi - \theta, \phi + \pi) = (-1)^l Y_{lm}(\theta, \phi) \tag{3.2}$$

and operated on by the $\mathcal{PT}$ operator

$$\mathcal{PT}[Y_{lm}(\theta, \phi)] = Y_{lm}^*(\pi - \theta, \phi + \pi) = (-1)^l Y_{lm}^*(\theta, \phi) \tag{3.3}$$

defining the $\mathcal{PT}$ symmetric spherical harmonics as

$$Y_{lm}^g(\theta, \phi) = e^g\ Y_{lm}(\theta, \phi) \tag{3.4}$$

where $g \equiv g(r, \theta, \phi)$ is any function and the inner product is given as

$$\langle Y^g_{l',m'}(\theta,\phi)|Y^g_{lm}(\theta,\phi)\rangle = \int d\Omega \; \mathcal{PT}[Y^g_{l',m'}(\theta,\phi)]Y^g_{lm}(\theta,\phi) \tag{3.5}$$

and also

$$\mathcal{PT}[Y^g_{l',m'}(\theta,\phi)] = e^{g(r,\pi-\theta,\phi+\pi)}(-1)^l Y^*_{lm}(\theta,\phi) \tag{3.6}$$

hence,

$$\langle Y^g_{l',m'}(\theta,\phi)|Y^g_{lm}(\theta,\phi)\rangle = (-1)^l \int d\Omega \; e^{[g^*(r,\pi-\theta,\phi+\pi)+g(r,\theta,\phi)]} Y^*_{l',m'}(\theta,\phi) Y_{lm}(\theta,\phi) \tag{3.7}$$

If the following condition [7, 8] is fulfilled,

$$e^{[g^*(r,\pi-\theta,\phi+\pi)+g(r,\theta,\phi)]} = \alpha \tag{3.8}$$

then

$$\langle Y^g_{l',m'}(\theta,\phi)|Y^g_{lm}(\theta,\phi)\rangle = (-1)^l \alpha \; \delta_{m,m'} \; \delta_{l,l'} \tag{3.9}$$

So it is observed that the spherical harmonics are orthogonal under $\mathcal{PT}$ transformation if eqn.(3.8) is satisfied.
Applying the $\mathcal{PT}$ transformation,

$$f(\theta,\phi) = \sum_{l\geq 0} \sum_{m=-l}^{l} C_{lm} Y^g_{lm}(\theta,\phi) \tag{3.10}$$

and applying the orthonormality conditions results in

$$C_{lm} = \frac{(-1)^l}{\lambda} \langle Y^g_{lm}(\theta,\phi)|f(\theta,\phi)\rangle = \frac{(-1)^l}{\lambda} \int d\Omega \mathcal{PT}[Y^g_{lm}(\theta,\phi) f(\theta,\phi) \tag{3.11}$$

So the $\mathcal{PT}$ symmetric hydrogen atom wave function can be defined as

$$\Psi^g_{nlm} = e^{g(r,\theta,\phi)} \Psi_{nlm} \tag{3.12}$$

where Ψ_{nlm} is defined in eqn.(2.1). For simplicity we will write this as

$$|nlm\rangle^g = e^g |nlm\rangle \tag{3.13}$$

and the complex conjugate as,

$$\langle nlm|^g = e^{g^*} \langle nlm| \tag{3.14}$$

3.0.3 $\mathcal{PT}$ Symmetric Angular Momentum

As defined, $g \equiv g(r, \theta, \phi)$, the angular momentum operator is [7]

$$L_i^g = e^g L_i e^{-g} \tag{3.15}$$

In general L_i^g is non-Hermitian, and their algebra is given as

$$[L_x^g, L_y^g] = iL_z^g, \qquad [L_z^g, L_x^g] = iL_y^g, \qquad [L_y^g, L_z^g] = iL_x^g \tag{3.16}$$

also,

$$(L^g)^2 = (L_x^g)^2 + (L_y^g)^2 + (L_z^g)^2, \qquad [(L^g)^2, L_i^g] = 0 \tag{3.17}$$

Similar to eqn.(2.14)

$$(L^g)^2 Y_{lm}^g(\theta, \phi) = l(l+1) Y_{lm}^g(\theta, \phi), \qquad Y_{lm}^g(\theta, \phi) = e^g Y_{lm}(\theta, \phi) \tag{3.18}$$

and similar to eqn.(2.9)

4 Transformations

If A, B and C are operators that satisfy commutation relations such as,

$$[A, B] = C \tag{4.1}$$

These operators transform as;

$$A^g = e^g A e^{-g}, \qquad B^g = e^g B e^{-g}, \qquad C^g = e^g C e^{-g} \tag{4.2}$$

now the commutation rules are,

$$[A^g, B^g] = C^g \tag{4.3}$$

Taking the transformation of the position and the momentum operator as

$$x_i^g = e^g x_i e^{-g}, \qquad p_i^g = e^g p_i e^{-g} \tag{4.4}$$

the following commutation rules using this transformation are given as,

$$[L_i^g, x_j] = i\epsilon_{ijk} x_k \tag{4.5}$$

$$[L_i^g, p_j] \neq i\epsilon_{ijk} p_k \tag{4.6}$$

and

$$[L_i^g, p_j^g] = i\epsilon_{ijk} p_k^g \tag{4.7}$$

Defining the Hamiltonian in the $\mathcal{PT}$ symmetric case as

$$H^g = e^g H e^{-g} \tag{4.8}$$

then the commutation relations with the Hamiltonian are given as,

$$[L_i, H^g] \neq 0 \tag{4.9}$$

and

$$[L_i^g, H^g] = 0 \tag{4.10}$$

So we see that L_i is a conserved quantity but L_i^g is not.

5 Core Softening with Lennard-Jones Potential

In mostly physics and chemistry, the Lennard-Jones potential is used and applied in a variety of ways. One particuler way is "Core Softening" by applying the Lennard Jones potential. This is a computational technique through which the Lennard-Jones potential is modified in a way that the repulsive part is softened or made less strong. By doing this we can make the particle-interactions overlap and pass through each other. Some applications of this technique is used in free energy calculations, modelling of soft matter such as colloids and softgels and in reaching structural equilibrium at a faster rate compared to the traditional Lennard-Jones potential.

Our future plan is to apply this methodology to a complex core softening method. In this methodology we plan on adding a complex term to the Lennard-Jones potential and study if it changes in the Non-Hermitian technique or remains the same. The effective potential will look like,

$$V_{eff}(r) = V_{LJ}(r) + i\delta V' \tag{5.1}$$

where iV' as the complex part in which δ shows the strength. We believe that there may be applications of this in areas such as many body simplification and the reaction rates of chemical reactions.

6 Conclusion

In this study we have described the basics of Non-Hermitian quantum mechanics briefly and proposed an idea which connects Non-Hermitian quantum mechanics and Lennard-Jones potential. Our future research is to develop a theoretical framework and a computational method through which we can study the applications of this technique. We welcome collaborations.

7 Conflict of Interest

The authors declare no conflict of interest.

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