Molecules as Riemannian Manifolds

M. Rahimi[*], M. Abbasi

*Department of Mathematics, Faculty of Science,
University of Qom, Qom, Iran.*

m10.rahimi@gmail.com , m.abbasi78@gmail.com

Abstract

In this paper, using the electronic charge densities, we assign a Riemannian manifold to any molecular system. Since we have many important quantities on a Riemannian Manifold, we may define them for molecular systems. A concept of distance on the configuration space of a molecule is defined. We also give a lower bound for the min square error of an unbiased estimator of molecular configurations.

1 Introduction

Mathematical modeling is applied to formulate the concepts related to theoretical chemistry such as molecular structures. Shannon information theory [1,2], Fisher information theory [3,4], theory of dynamical systems [5] and catastrophe theory [6] are some branches of mathematics that are applied in modeling of theoretical chemistry.

Collard and Hall [7] applied scalar functions and their corresponding gradient systems to introduce molecular structures. In this case, the electron density functions are the scalar functions. Then, Bader et al. [8–10] applied the formulation of Collard and Hall in quantum theory of atoms in molecules (abbreviated in QTAIM).

This paper is an attempt to apply information geometry techniques [11] in modeling the molecular structures. We assign a Riemannian manifold to any molecular system. We may apply the tools in Riemannian geometry to define some geometric concepts for

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[*]Corresponding author.

molecular structures. For instance, we define a metric on the nuclear configuration space of a molecule which is based on the information theoretical aspects of the electron charge densities of a molecule rather than the dynamical aspects [12].

2   Electron charge density and configuration space

To understand the connection between electron charge density and a parameterization space, one needs to consider Schrödinger equation. As a quantum system, each state of a molecular system is described by a state function Ψ in a Hilbert space. This function satisfies the Schrödinger equation

$$\{\hat{H} - E\}\Psi = 0$$

where

$$\hat{H} = \left(-\frac{\hbar^2}{2m}\right)\sum_{i=1}^{N}\nabla_i^2 + \left(-\frac{\hbar^2}{2M}\right)\sum_{j=1}^{L}\nabla_j^2 + \hat{V}_{en} + V_{ee} + V_{nn} \tag{2.1}$$

is the Hamilton operator, $V = \hat{V}_{en} + V_{ee} + V_{nn}$ the total potential operator, m, N the mass and number of electrons respectively, M, L the mass and number of nuclei respectively, and E the total energy of the system.

Since the exact solution of the Schrödinger equation may not be given in general, the solution of this equation is given using approximation methods. In Born-Oppenheimer approximation, nuclei are considered as static charges. In this case, the terms of kinetic energy of nuclei are ignored in the Hamiltonian of the molecular system, so (2.1) reduces to

$$\hat{H}_e = \left(-\frac{\hbar^2}{2m}\right)\sum_{i=1}^{N}\nabla_i^2 + \hat{V}_{en} + V_{ee}, \tag{2.2}$$

which is called the electron Schrödinger equation. This process leads to the parameterization of the states of the molecular system. Indeed, the eigenvalue problem corresponding to the operator (2.2), is as follows:

$$\{\hat{H}_e - E_e\}\Psi(x_1, x_2, \cdots, x_n, \xi) = 0. \tag{2.3}$$

Therefore, the electron charge density also depends on the parameter ξ, where ξ stands for the position or geometry of nuclei in Born-Oppenheimer approximation. The electron charge density is defined as follows:

$$\rho_\xi(r) = N\sum_{\text{spin}}\int_{\text{space}}\Psi^*(x_1, x_2, \cdots, x_n, \xi)\delta(r - r_1)\Psi(x_1, x_2, \cdots, x_n, \xi)dr_1 \cdots dr_N \tag{2.4}$$

where δ is the Dirac function and $x_i = (r_i, s_i)$ $(i = 1, 2, \cdots, N)$ is the space-spin coordinate. So, any molecule corresponds to a family of electron charge densities $\{\rho_\xi\}_\xi$ which may be used to define the concept of molecular structure [8, 10].

3 Molecular manifold

Let M be a molecular system. By the previous discussions, let $\Theta \subset \mathbb{R}^n$ be the space of all nuclear configurations of the molecular system M, and $S = \{\rho_\xi\}_{\xi \in \Theta}$ be the family of all electron charge densities of M defined in (2.4). In other words, for any $\xi \in \Theta$, $\rho_\xi : \Omega \subset \mathbb{R}^n \to [0, 1]$ is a probability distribution function and

$$S = \{\rho_\xi = \rho(r, \xi) : \quad \xi = (\xi_1, \xi_2, \cdots, \xi_n) \in \Theta\}.$$

Note that, the mapping $\xi \longmapsto \rho_\xi$ is an injection. It is also assumed that ρ_ξ $(\xi = (\xi_1, \xi_2, \cdots, \xi_n))$ is smooth with respect to the components ξ_i $(i = 1, 2, \cdots, n)$, i. e., the function $\xi \longmapsto \rho_\xi$ is C^∞. Let also $\Theta \subset \mathbb{R}^n$ be an open set. So, all the terms of the form $\frac{\partial \rho_\xi}{\partial \xi_i}$ and $\frac{\partial^2 \rho_\xi}{\partial \xi_i \partial \xi_j}$ are well-defined on Θ and we have

$$\int_\Omega \frac{\partial \rho_\xi}{\partial \xi_i}(r) dr = \frac{\partial}{\partial \xi_i} \int_\Omega \rho_\xi(r) dr = \frac{\partial}{\partial \xi_i}(1) = 0.$$

The mapping $\phi : S \to \mathbb{R}^n$ defined by $\phi(\rho_\xi) = \xi$ gives a coordinate system $\phi = [\xi_i]$ on S which makes it a manifold with one single local chart. On the other hand, if $\psi : \Theta \to \psi(\Theta) \subset \mathbb{R}^n$ is another C^∞-diffeomorphism, then $\eta = \psi(\xi)$ is another coordinate system for S, and indeed $S = \{\rho_{\psi^{-1}(\eta)}\}_{\eta \in \psi(\Theta)}$. Based on the previous discussions, S is a C^∞-manifold, where each parameterization of S is indeed a coordinate system. S is called the *molecular manifold* of M. Now, we define a Riemannian metric on $S = \{\rho_\xi\}_\xi$ corresponding to the molecule M. The Fisher information matrix $G(\xi) = [g_{ij}(\xi)]_{n \times n}$ $(\xi \in \Theta)$ is defined by

$$g_{ij}(\xi) = \int_\Omega \rho_\xi(r) \frac{\partial l}{\partial \xi_i}(r) \frac{\partial l}{\partial \xi_j}(r) dr \tag{3.1}$$

where $l = l_\xi(r) = \log \rho_\xi(r)$ [11].

The functions $g_{ij} : \Theta \to \mathbb{R}^\infty$ are C^∞. Note that, using the correspondence $\xi \longmapsto \rho_\xi$, each g_{ij} may be considered as a function defined on S. We have:

1. $G(\xi)$ is a symmetric matrix, since

$$\forall \xi \in \Theta \quad g_{ij}(\xi) = g_{ji}(\xi) \quad (i, j = 1, 2, \cdots, n).$$

2. $G(\xi)$ is semi positive-definite, since, for every given $V = (v_1, v_2, \cdots, v_n)^t$ we have:

$$V^t G(\xi) V = \sum_{i,j} v_i v_j g_{ij}(\xi) = \int_\Omega \left(\sum_{i=1}^n v_i \frac{\partial l}{\partial \xi_i}(r) \right)^2 dr \geq 0.$$

Now, the inner product $< \cdot, \cdot >$ on the tangent space TS is defined as follows:

$$g_{ij} = < \partial_i, \partial_j > \tag{3.2}$$

where $\partial_i = \frac{\partial}{\partial \xi_i}$. Clearly, the Riemannian metric $g = < \cdot, \cdot >$ is uniquely determined by (3.2). So, (S, g) is a Riemannian manifold corresponding to the molecule M.

A natural question one may ask is: what is the advantage of looking at a molecule as a Riemannian manifold? The answer refers to the structural potentials that Riemannain manifolds own. On a Riemannian manifold, we have a differential structure, an inner product, an induced metric and geodesics as well as many other useful concepts such as connections, curvature and torsion tensors and so on. All these geometric concepts may be injected into the theory of molecular systems to enrich this part of theoretical chemistry. As an example, we apply the inner product defined in (3.2) to introduce a distance between nuclear configurations of a molecule.

3.1 Fisher distance

Let $S = \{\rho_\xi\}_{\xi \in \Theta}$ be the molecular manifold corresponding to a molecule M. For any C^1-curve $\gamma : [0, 1] \to S$, the length of γ is given by

$$L(\gamma) := \int_0^1 \sqrt{\sum_{i,j} g_{ij} \dot{\gamma}_i \dot{\gamma}_j} dt. \tag{3.3}$$

Now, let $\xi, \eta \in \Theta$ be two nuclear configurations of M. The set of all C^1 curves $\gamma : [0, 1] \to S$ such that $\gamma(0) = \rho_\xi$ and $\gamma(1) = \rho_\eta$ is denoted by $\Delta_{\xi\eta}$. The Fisher distance between ξ and η is defined as

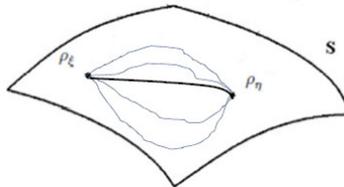$$d_F(\xi, \eta) := \inf\{L(\gamma) : \gamma \in \Delta_{\xi\eta}\}. \tag{3.4}$$

Figure 1. Molecular manifold and curves between two points on it

Clearly $d_F : \Theta \times \Theta \to [0, +\infty)$ is a metric on the space of nuclear configurations of M, i. e.,

1. $d_F(\xi, \eta) \geq 0$ for all $\xi, \eta \in \Theta$, and $d_F(\xi, \eta) = 0$ if and only if $\xi = \eta$.

2. $d_F(\xi, \eta) = d_F(\eta, \xi)$ for all $\xi, \eta \in \Theta$.

3. $d_F(\xi, \eta) \leq d_F(\xi, \zeta) + d_F(\zeta, \eta)$ for all $\xi, \eta, \zeta \in \Theta$.

Formula (3.4) is not suitable for practical and computational aspects, since the infimum is taken over an infinite (even more on an uncountable) set. To resolve this difficulty, we need to have some suitable connection on S.

3.2 Christoffel symbols and connection of a molecule

Let $S = \{\rho_\xi\}_{\xi \in \Theta}$ be the molecular manifold corresponding to a molecule M. For $\xi \in \Theta$, let $l_\xi := \log \rho_\xi$. The functions $\Gamma_{ij}^k : \Theta \to \mathbb{R}$ defined by

$$\left(\Gamma_{ij}^k\right)_\xi := \int_\Omega \rho_\xi(r) \partial_k l_\xi \left(\partial_i \partial_j l_\xi + \frac{1}{2} \partial_i l_\xi \partial_j l_\xi\right) dr$$

are called the Christiffel symbols of the molecule M. Now, the connection ∇ on S is defined as follows:

$$< \nabla_{\partial_j}^{\partial_i}, \partial_k >= \Gamma_{ij}^k$$

where $g = < \cdot, \cdot >$ is the Fisher metric of the molecule M. Clearly, ∇ is a symmetric connection. Also,

$$
\begin{aligned}
(\partial_k g_{ij})_\xi &= \partial_k \left(\int_\Omega \rho_\xi(r) \partial_i l_\xi \partial_j l_\xi dr\right) \\
&= \int_\Omega (\partial_k \rho_\xi(r) \partial_i l_\xi \partial_j l_\xi + \rho_\xi(r) \partial_k \partial_i l_\xi \partial_j l_\xi + \rho_\xi(r) \partial_i l_\xi \partial_k \partial_j l_\xi)\, dr \\
&= \left(\Gamma_{ij}^k\right)_\xi + \left(\Gamma_{ji}^k\right)_\xi.
\end{aligned}
$$

Briefly,

$$\partial_k g_{ij} = \Gamma_{ij}^k + \Gamma_{ji}^k. \tag{3.5}$$

By (3.5) and the equality $\Gamma_{ij}^k = \Gamma_{ji}^k$ we will have the following theorem [11]:

Theorem 3.1 ∇ *is a Levi-Civita connection with respect to the Fisher metric* $g = < \cdot, \cdot >$.

By the previous discussions, to determine the distance between two nuclear configurations $\xi, \eta \in \Theta$ of a molecule M, one should solve the following geodesic differential equations:

$$\ddot{\gamma}^k(t) + \sum_{i,j=1}^n \Gamma_{ij}^k(\gamma(t)) \dot{\gamma}^i(t) \dot{\gamma}^j(t) = 0 \qquad (1 \leq k \leq n). \tag{3.6}$$

4 Molecular manifold of hydrogen molecular ion

In this section, we consider the hydrogen molecular ion H_2^+ and apply the discussion in section 3. This molecule is composed of two protons and an electron.

4.1 A one-dimensional molecular manifold

In lights of Born-Oppenheimer approximation, the nuclei of H_2^+ are assumed to have constant distance ξ. So, it suffices to consider the electron Schrödinger equation. The Hamiltonian of the system is

$$\hat{H}_e = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B} + \frac{e^2}{4\pi\epsilon_0 \xi}$$

where r_A and r_B are the distances of the electron from the nuclei A and B respectively.
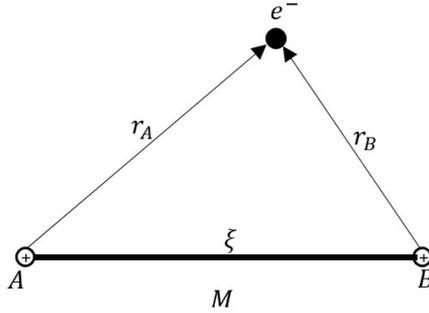

Figure 2. A configuration of the hydrogen molecular ion.

We consider the following approximate wave function for the electron Schrödinger equation $\hat{H}_e\Psi = E_e\Psi$:

$$\Psi = a_0^{-\frac{3}{2}}\pi^{\frac{-1}{2}}\left(\eta_A e^{-\frac{r_A}{a_0}} + \eta_B e^{-\frac{r_B}{a_0}}\right)$$

where $a_0 = 0.53\text{Å}$ is the Bohr radius, and η_A and η_B are constant coefficients. Since the nuclei are the same, we may assume that $\eta_A = \eta_B = \eta$, so, the electron charge density function is as follows:

$$\begin{aligned}
\rho = \Psi^2 &= a_0^{-3}\pi^{-1}\eta^2\left(e^{-\frac{r_A}{a_0}} + e^{-\frac{r_B}{a_0}}\right)^2 \\
&= a_0^{-3}\pi^{-1}\eta^2\left(e^{-\frac{2r_A}{a_0}} + e^{-\frac{2r_B}{a_0}} + 2e^{-\frac{r_A+r_B}{a_0}}\right)
\end{aligned}$$

Now, set the atom A on the origin and the atom B on the positive direction of the y-axis, so, in Cartesian coordinate

$$r_A = \sqrt{x^2 + y^2 + z^2}, \quad r_B = \sqrt{x^2 + (y-\xi)^2 + z^2}$$

Therefore,

$$\rho_\xi(x, y, z) = a_0^{-3}\pi^{-1}\eta^2 \left(e^{-\frac{\sqrt{x^2+y^2+z^2}}{a_0}} + e^{-\frac{\sqrt{x^2+(y-\xi)^2+z^2}}{a_0}} \right)^2 \tag{4.1}$$

Now, we apply the condition $\int_{\mathbb{R}^3} \rho_\xi d\tau = 1$, therefore,

$$a_0^{-3}\pi^{-1}\eta^2 \left(\int_{\mathbb{R}^3} e^{-\frac{2r_A}{a_0}} d\tau + \int_{\mathbb{R}^3} e^{-\frac{2r_B}{a_0}} d\tau + 2\int_{\mathbb{R}^3} e^{-\frac{r_A+r_B}{a_0}} d\tau \right) = 1. \tag{4.2}$$

By the definition of Bohr radius, we may replace $\mathbb{R}^3$ by

$$D = \{(x, y, z) \in \mathbb{R}^3 : \quad x^2 + y^2 + z^2 \leq 2a_0\}$$

in the three integrals in (4.2), so one may write

$$I_1 := \int_{\mathbb{R}^3} e^{-\frac{2r_A}{a_0}} d\tau \simeq \int_D e^{-\frac{2r_A}{a_0}} d\tau, \quad I_2 := \int_{\mathbb{R}^3} e^{-\frac{2r_B}{a_0}} d\tau \simeq \int_D e^{-\frac{2r_B}{a_0}} d\tau,$$

$$I_3 := \int_{\mathbb{R}^3} e^{-\frac{r_A+r_B}{a_0}} d\tau \simeq \int_D e^{-\frac{r_A+r_B}{a_0}} d\tau \tag{4.3}$$

If we set $Q(\xi) := I_1 + I_2 + I_3 = \int_D \left(e^{-\frac{r_A}{a_0}} + e^{-\frac{r_B}{a_0}} \right)^2 d\tau$ then, by (4.2)

$$\eta^2 = \frac{\pi a_0^3}{Q(\xi)}$$

and the electron charge density of the molecular ion H_2^+ is of the form

$$\rho_\xi = Q(\xi)^{-1} \left(e^{-\frac{r_A}{a_0}} + e^{-\frac{r_B}{a_0}} \right)^2 = Q(\xi)^{-1} \left(e^{-\frac{\sqrt{x^2+y^2+z^2}}{a_0}} + e^{-\frac{\sqrt{x^2+(y-\xi)^2+z^2}}{a_0}} \right)^2 \tag{4.4}$$

So, in this case, the molecular manifold corresponding to H_2^+ is a one-dimensional manifold with the parameter ξ in the configuration space

$$\Theta = (0, 2a_0) = (0, 1.06\mathring{A}) \subset \mathbb{R}.$$

Now, we may calculate the only Fisher coefficient $g(\xi) = g_{11}(\xi)$ and Christoffel coefficient $\Gamma(\xi) = \Gamma_{11}^1(\xi)$ for H_2^+. A direct calculation results in

$$\frac{\left(\frac{\partial\rho_\xi}{\partial\xi}\right)^2}{\rho_\xi} = \frac{Q'(\xi)^2 Q(\xi)^{-2} \left(e^{-\frac{r_A}{a_0}} + e^{-\frac{r_B}{a_0}} \right)^2 + \frac{4}{a_0^2} e^{-\frac{2r_B}{a_0}} \frac{(y-\xi)^2}{r_B^2} + \frac{4}{a_0} Q'(\xi)\frac{y-\xi}{r_B} \left(e^{-\frac{r_A}{a_0}} + e^{-\frac{r_B}{a_0}} \right)}{Q(\xi)}$$

where

$$r_A = \sqrt{x^2 + y^2 + z^2}, \quad r_B = \sqrt{x^2 + (y - \xi)^2 + z^2}.$$

Therefore,

$$g(\xi) = \int_D \frac{\left(\frac{\partial \rho_\xi}{\partial \xi}\right)^2}{\rho_\xi} d\tau = \frac{Q'(\xi)^2 Q(\xi)^{-1} + \frac{4}{a_0^2} R(\xi) + \frac{4}{a_0} Q'(\xi) S(\xi)}{Q(\xi)}$$

or equivalently,

$$g(\xi) = \left(\frac{Q'(\xi)}{Q(\xi)}\right)^2 + \frac{4}{a_0^2} \frac{R(\xi)}{Q(\xi)} + \frac{4}{a_0} \frac{Q'(\xi) S(\xi)}{Q(\xi)} \tag{4.5}$$

where

$$R(\xi) = \int_D \frac{(y-\xi)^2}{r_B^2} e^{-\frac{2r_B}{a_0}} d\tau \tag{4.6}$$

and

$$S(\xi) = \int_D \frac{y-\xi}{r_B} \left(e^{-\frac{r_A}{a_0}} + e^{-\frac{r_B}{a_0}}\right) d\tau. \tag{4.7}$$

Finally,

$$\Gamma(\xi) = \frac{1}{2} \frac{\partial}{\partial \xi} g(\xi) \tag{4.8}$$

where $g(\xi)$ is given by (4.5).

4.2 Numerical approximations

In the previous subsection, we presented a formula for $g(\xi)$ and $\Gamma(\xi)$ in terms of the integrals $Q(\xi), R(\xi)$ and $S(\xi)$. In this subsection, we use some numerical methods to approximate $Q(\xi), R(\xi)$ and $S(\xi)$. To do this, we first write these integrals in spherical coordinates. Using the spherical coordinates $x = \rho \cos\theta \sin\phi$, $y = \rho \sin\theta \sin\phi$ and $z = \rho \cos\phi$, we will have:

$$Q(\xi) = \int_0^{2\pi} \int_0^{\pi} \int_0^{2a_0} \left(e^{-\frac{\rho}{a_0}} + e^{-\frac{\sqrt{\rho^2 - 2\xi\rho \sin\theta \sin\phi + \xi^2}}{a_0}}\right)^2 \rho^2 \sin\phi \, d\rho \, d\phi \, d\theta, \tag{4.9}$$

$$R(\xi) = \int_0^{2\pi} \int_0^{\pi} \int_0^{2a_0} \frac{(\rho \sin\theta \sin\phi - \xi)^2 \rho^2 \sin\phi}{\rho^2 - 2\xi\rho \sin\theta \sin\phi + \xi^2} e^{-\frac{2\sqrt{\rho^2 - 2\xi\rho \sin\theta \sin\phi + \xi^2}}{a_0}} d\rho \, d\phi \, d\theta, \tag{4.10}$$

$$S(\xi) = \int_0^{2\pi} \int_0^{\pi} \int_0^{2a_0} \frac{(\rho \sin\theta \sin\phi - \xi)\rho^2 \sin\phi}{\sqrt{\rho^2 - 2\xi\rho \sin\theta \sin\phi + \xi^2}} \left(e^{-\frac{\rho}{a_0}} + e^{-\frac{\sqrt{\rho^2 - 2\xi\rho \sin\theta \sin\phi + \xi^2}}{a_0}}\right) d\rho \, d\phi \, d\theta.$$
(4.11)

Using numerical methods, one can calculate g and Γ numerically at every point ξ.

Remark 4.1 *One should note that, we may calculate the integrals $Q(\xi)$, $R(\xi)$ and $S(\xi)$ using other coordinate systems such as confocal elliptic coordinates. However we use MATLAB* `integral3` *function to approxmate these integrals which is accurate upto 10^{-6} angsrtom.*

To plot the functions g and Γ in figure 3, we calculate these functions at 501 equally space points as $\xi_i = i\frac{2a_0}{500}$ for $i = 0, \cdots, 500$ by using `integral3` function of MATLAB software. Using these 501 equally space points and clamped cubic spline interpolation method, we can find cubic spline approximation g_s of g by `spline` function of MATLAB.
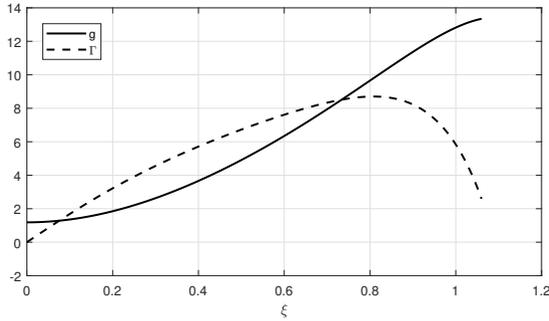

Figure 3. Plots of g and Γ obtained by calculating these functions at 501 equally-space points.

To solve the differential equation

$$\begin{cases} \ddot{\gamma}(t) + \Gamma(\gamma(t))(\dot{\gamma}(t))^2 = 0 \\ \gamma(0) = \xi_1, \quad \gamma(1) = \xi_2 \end{cases} \tag{4.12}$$

where $0 \le \xi_1, \xi_2 \le 2a_0$, set $z = \frac{d\gamma}{dt}$ then $\frac{d^2\gamma}{dt^2} = z\frac{dz}{d\gamma}$. By this substitution, the differential equation (4.12) is converted to

$$z\frac{dz}{d\gamma} + \Gamma(\gamma)z^2 = 0 \tag{4.13}$$

If $z = 0$ then $\gamma(t)$ is a constant function. This solution is acceptable only when $\gamma(0) = \gamma(1)$. Now suppose $z \ne 0$, dividing the differential equation (4.13) by z, we can obtain a separable differential equation as

$$\frac{dz}{d\gamma} + \Gamma(\gamma)z = 0 \tag{4.14}$$

This equation has the general solution $\ln(z) = \int -\Gamma(\gamma)\,d\gamma = -\frac{1}{2}g(\gamma) + C_1$, so we have

$$\frac{d\gamma}{dt} = z = \pm e^{C_1}e^{-0.5g(\gamma)} \tag{4.15}$$

Since exponential function is always positive, the sign of $\frac{d\gamma}{dt}$ doesn't change on interval $[0, 2a_0]$ and γ is an increasing function if positive sign is chosen in (4.15) and decreasing function if negative sign is chosen. Now, suppose that $\gamma(0) = \xi_1 < \xi_2 = \gamma(1)$ and therefore

γ is not a decreasing function, so we may choose the positive sign in (4.15) and solve that equation. We have

$$\begin{cases} \gamma(t) = e^{C_1} \int_0^t e^{-0.5g(\gamma(x))} \, dx + C_2 \\ \gamma(0) = \xi_1 < \xi_2 = \gamma(1) \end{cases} \tag{4.16}$$

Applying $\gamma(0) = \xi_1$ on (4.16) will result in

$$\begin{cases} \gamma(t) = e^{C_1} \int_0^t e^{-0.5g(\gamma(x))} \, dx + \xi_1 \\ \gamma(0) = \xi_1 < \xi_2 = \gamma(1) \end{cases} \tag{4.17}$$

To find the function γ from (4.17) approximately, we choose $n + 1$ equally space points $t_i = \frac{i}{n}$ for $i = 0, 1, \cdots, n$, and we have

$$\gamma(t_i) = e^{C_1} \int_0^{t_i} e^{-0.5g(\gamma(x))} \, dx + \xi_1, \quad \forall i = 0, 1, \cdots, n \tag{4.18}$$

So we can write

$$\gamma(t_i) = \gamma(t_{i-1}) + e^{C_1} \int_{t_{i-1}}^{t_i} e^{-0.5g(\gamma(x))} \, dx, \quad \forall i = 1, \cdots, n \tag{4.19}$$

where $\gamma(t_0) = \xi_1$. Using trapezoidal rule of numerical integration, we have

$$\int_{t_{i-1}}^{t_i} e^{-0.5g(\gamma(x))} \, dx \approx \frac{1}{2n} \left(e^{-0.5g(\gamma(t_{i-1}))} + e^{-0.5g(\gamma(t_i))} \right). \tag{4.20}$$

Substitution of equation (4.20) in (4.19) leads to

$$\gamma(t_i) \approx \gamma(t_{i-1}) + e^{C_1} \frac{1}{2n} \left(e^{-0.5g(\gamma(t_{i-1}))} + e^{-0.5g(\gamma(t_i))} \right), \quad \forall i = 1, \cdots, n \tag{4.21}$$

Since $\gamma(t_n) = \gamma(1) = \xi_2$, there are n unknown parameters $C_1, \gamma(t_1), \gamma(t_2), \cdots, \gamma(t_{n-1})$ and n non-linear equations in (4.21). We set $n = 1000$ and use `fsolve` function of MATLAB to find approximately $C_1, \gamma(t_1), \gamma(t_2), \cdots, \gamma(t_{n-1})$ from n equations in (4.21). Then, we use five point numerical differentiation method to find $\gamma'(t_0), \gamma'(t_1), \cdots, \gamma'(t_n)$. Using these points, we approximate the functions γ and γ' by cubic spline interpolations γ_s and γ'_s respectively.

Applying (3.3), for the one-dimensional manifold corresponding to the hydrogen molecular ion, the length of the geodesic curve $\gamma(t)$ where $\gamma(0) = \xi_1$ and $\gamma(1) = \xi_2$ is

$$d_F(\xi_1, \xi_2) = \int_0^1 |\gamma'(t)| \sqrt{g(\gamma(t))} dt. \tag{4.22}$$

Using the approximations γ_s, γ'_s and g_s of γ, γ' and g respectively, one can find $d_F(\xi_1, \xi_2)$ numerically, for every $0 \leq \xi_1, \xi_2 \leq 2a_0$.

Remark 4.2 *If $\xi_1 > \xi_2$, one can choose the negative sign in differential equation (4.15) and repeat the mentioned process to find γ.*

In figures 4 and 5, the plots and lengths of some γ functions, for $\xi_1 = 0$ and $\xi_1 = 0.5$ respectively, are given (in these figures $\xi_2 = 0, 0.1, \cdots, 1$).

In figure 6 we give $d_F(\xi_1, \xi_2)$ for $\xi_1, \xi_2 = 0, 0.1, \cdots, 1, 2a_0$ in a table.
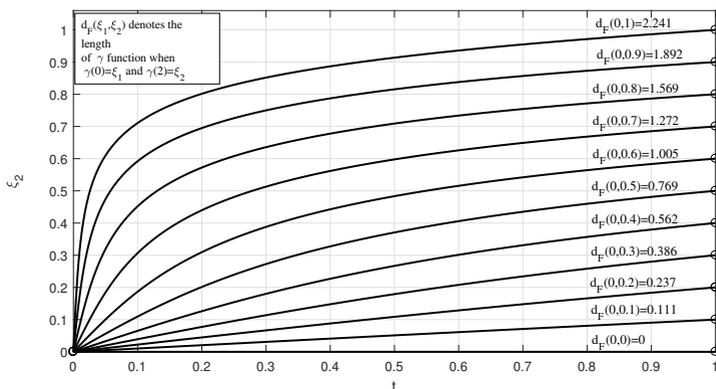

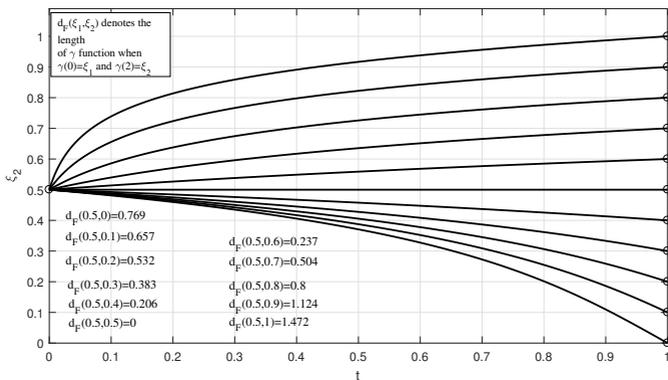**Figure 4.** Plots and lengths of some functions γ for $\xi_1 = 0$ and $\xi_2 = 0, 0.1, \cdots, 1$.

Figure 5. Plots and lengths of some functions γ for $\xi_1 = 0.5$ and $\xi_2 = 0, 0.1, \cdots, 1$.

ξ_1 \ ξ_2	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1	$2a_0$
0	0	0.1115	0.237	0.3857	0.5624	0.7688	1.0055	1.2723	1.5687	1.893	2.2412	2.4589
0.1	0.1115	0	0.1255	0.2743	0.4509	0.6573	0.894	1.1609	1.4572	1.7815	2.1298	2.3473
0.2	0.237	0.1255	0	0.1488	0.3254	0.5318	0.7685	1.0354	1.3317	1.656	2.0042	2.2215
0.3	0.3857	0.2743	0.1488	0	0.1766	0.383	0.6197	0.8866	1.183	1.5072	1.8555	2.0727
0.4	0.5624	0.4509	0.3254	0.1766	0	0.2064	0.4431	0.71	1.0064	1.3306	1.6788	1.8961
0.5	0.7688	0.6573	0.5318	0.383	0.2064	0	0.2367	0.5036	0.8	1.1242	1.4725	1.6897
0.6	1.0055	0.894	0.7685	0.6197	0.4431	0.2367	0	0.2669	0.5633	0.8875	1.2358	1.453
0.7	1.2723	1.1609	1.0354	0.8866	0.71	0.5036	0.2669	0	0.2964	0.6206	0.9689	1.1861
0.8	1.5687	1.4572	1.3317	1.183	1.0064	0.8	0.5633	0.2964	0	0.3242	0.6725	0.8898
0.9	1.893	1.7815	1.656	1.5072	1.3306	1.1242	0.8875	0.6206	0.3242	0	0.3483	0.5655
1	2.2412	2.1298	2.0042	1.8555	1.6788	1.4725	1.2358	0.9689	0.6725	0.3483	0	0.2173
$2a_0$	2.4589	2.3473	2.2215	2.0727	1.8961	1.6897	1.453	1.1861	0.8898	0.5655	0.2173	0

Figure 6. Table of $d_F(\xi_1, \xi_2)$ for $\xi_1, \xi_2 = 0, 0.1, \cdots, 1, 2a_0$.

5 Estimation error

Suppose that $S = \{\rho_\xi\}_{\xi \in \Theta}$ is an n-dimensional molecular manifold corresponding to a molecule M. Suppose that a data is randomly generated subject to an electron density function ρ_ξ in S. Consider the problem of estimating the unknown configuration $\xi \in \Theta$ by a function $\hat{\xi} : \Omega \to \mathbb{R}^n$ which is called an estimator. $\hat{\xi} = (\hat{\xi}_1, \hat{\xi}_2, \cdots, \hat{\xi}_n)$ is called an unbiased estimator if

$$E_\xi(\hat{\xi}) = \xi \qquad \forall \xi \in \Theta$$

where

$$E_\xi(\hat{\xi}) = \int_\Omega \hat{\xi}(r)\rho_\xi(r)d\tau.$$

For a configuration $\hat{\xi} = (\hat{\xi}_1, \hat{\xi}_2, \cdots, \hat{\xi}_n) \in \Theta$, the mean square error matrix of an unbiased estimator $\hat{\xi}$ is defined by $V(\xi) = (v_{ij}(\xi))_{n \times n}$ where

$$v_{ij}(\xi) = E_\xi \left[(\hat{\xi}_i - \xi_i)(\hat{\xi}_i - \xi_i) \right].$$

A better estimation of a nuclear configuration ξ occurs if each $v_{ij}(\xi)$ is as small as possible. Cramer-Rao inequality states that the mean square error can not be as small as we like.

Equivalently, there is a lower bound for it which is related to the Fisher metric.

Theorem 5.1 *(Cramer-Rao inequality [11]) Let $\hat{\xi}$ be an unbiased estimator and $V(\xi) = (v_{ij}(\xi))_{n \times n}$ be the mean square error matrix. Then $V(\xi) \geq G(\xi)^{-1}$ in the sense that $V(\xi) - G(\xi)^{-1}$ is a positive semi-definite matrix.*

Now, we apply the Cramer-Rao inequality for the one-dimensional molecular manifold of H_2^+. Clearly, in this case, the mean square error matrix has only one array $v(\xi) = v_{11}(\xi)$, and is given by

$$v(\xi) = E_\xi \left[(\hat{\xi} - \xi)^2 \right]$$

and the Cramer-Rao inequality will be as follows:

$$v(\xi) \geq g(\xi)^{-1}$$

where $g(\xi)$ is given by (4.5). Consequently, since g is an increasing function, any unbiased estimation of a configuration $\xi \in \Theta$ of the molecule H_2^+ has a mean square error bounded below by

$$e(\xi) = \frac{Q(\xi)}{Q'(\xi)^2 Q(\xi)^{-1} + \frac{4}{a_0^2} R(\xi) + \frac{4}{a_0} Q'(\xi) S(\xi)} \geq \frac{1}{g(2a_0)} = 0.0749.$$
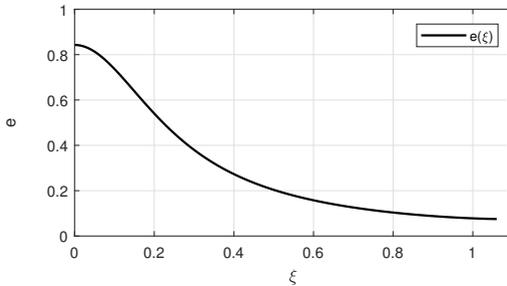
The graph of $e(\xi)$ is represented in Figure 7.

Figure 7. Plot of $e(\xi)$.

6 Summary and discussion

In this paper, a mathematical modeling of molecular systems is presented, using information geometry techniques. In this regard, we have assigned a Riemannian manifold to a molecular system which made us capable to define a metric on the nuclear configuration

space. Numerical methods are also applied to calculate the distance between some configurations of the molecule H_2^+. Finally, using Cramer-Rao inequality, we gave a lower bound for the mean square error of any unbiased estimator of the nuclear configurations of H_2^+.

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