

A new algorithm for rigid body molecular dynamics

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Abstract

The molecular dynamics of a completely rigid molecule is described in terms of external coordinates, namely translations and rotations, and a new algorithm is proposed, which is faster than other known methods and satisfies the constraints up to a desired accuracy. The procedure dispenses with the adoption of Lagrange multipliers and it is derived from an expression previously proposed for the motion of a semirigid molecule, when constraints are imposed to any selected number of intramolecular parameters. The latter need not to be specified for a rigid body but cannot be altogether ignored since it is necessary to guarantee that internal and external coordinates form a complete set of independent variables. This requirement is met by the familiar Eckart–Sayvetz conditions which provide with an iterative procedure for the evaluation, through symmetric orthogonalization, of a matrix of rotation. It turns out that only a first approximation of this matrix is necessary, therefore a final algorithm is proposed, based on the definition of infinitesimal angles of rotation about the mass center.

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1. Introduction

This paper deals with the molecular dynamics (MD) of a system of interacting rigid molecules undergoing intermolecular forces. Only external, namely translational and rotational, degrees of freedom are thus allowed, since through the whole simulation all intramolecular distances and angles are forced to maintain constant values. Because of these kinematical restrictions there is no need to consider internal degrees of freedom but actually they cannot be ignored since it is necessary to guarantee that internal and external displacements form a complete set of independent variables. This requirement leads to the Eckart–Sayvetz (ES) conditions [1,2] familiar to molecular spectroscopists and it is one of the objectives of this paper to show that they determine the amount of rotation of a molecule constrained to be rigid.

The MD of a rigid molecule has been explicitly considered in Ref. [3], using Lagrange multipliers, and may be

also treated with the procedure of Ref. [4], which is addressed to a semirigid molecule but obviously covers the case when all internal degrees of freedom are constrained. Both procedures use the position Verlet algorithm and require the inversion of a large, symmetric matrix which must be carried out only once, at the beginning of the simulation, but may become a problem for a very large molecule. Such inversion is not necessary in the procedure proposed here, which derives from the results of Ref. [4], exploits the ES conditions and is faster than the two above mentioned methods.

A short outline of the previous algorithms for the MD of a rigid molecule is presented in Section 2, the ES conditions are summarized in Section 3, the properties of the space of displacements are discussed in Section 4 and a new algorithm is presented in Section 5. The results are discussed in Section 6 and compared with those obtained with the above mentioned iterative procedures, with the symplectic splitting method of Ref. [5] and with the leapfrog scheme of Ref. [6]. A succinct summary is given in the [Appendix](#) for an iterative procedure to calculate a rotation matrix for a molecule constrained to be rigid.

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2. Previous algorithms for rigid molecules

In the method of linear constraints [3] a minimal atomic set is selected, formed by four non-coplanar atoms numbered 1, 2, 3, 4 in what follows, which define an oblique coordinate system with origin on atom 1 and three basic vectors $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$ pointing to atoms 2, 3, 4, respectively. Through all the paper we shall adopt the summation convention over repeated literal suffixes in a single term or algebraic expression. Therefore, letting X_{is} be the s th Cartesian coordinates of the i th atom measured in a space-fixed frame \mathbf{i} , the vectors of the oblique basis are related to the reference frame by the transformation

$$\mathbf{e}_\mu \equiv \mathbf{r}_{1(\mu+1)} = \mathbf{i}_s (X_{(\mu+1)s} - X_{1s}) \quad \mu = 1, 2, 3$$

The customary notation with upper and lower suffixes is adopted for covariant and contravariant vectors, therefore the metric tensor of the oblique basis has components given by

$$g_{\mu\nu} = \mathbf{e}_\mu \cdot \mathbf{e}_\nu \quad g^{\mu\nu} = \mathbf{e}^\mu \cdot \mathbf{e}^\nu \quad \text{such that } g_{\mu\alpha} g^{\alpha\nu} = \delta_{\mu\nu}$$

where $\mathbf{e}^\mu = g^{\mu\nu} \mathbf{e}_\nu$ are the reciprocal vectors. The rigid body procedure is based on a set of constraints imposed to the six distances $r_{12}, r_{13}, \dots, r_{34}$ among the atoms of the minimal set. A radius vector from the origin to any further atom $\alpha = 5, 6, 7, \dots$ is then expanded in the oblique basis as

$$\mathbf{r}_{1\alpha} = q^1 \mathbf{e}_1 + q^2 \mathbf{e}_2 + q^3 \mathbf{e}_3 \quad \text{with } q^\mu = \mathbf{r}_{1\alpha} \cdot \mathbf{e}^\mu$$

where q^μ are contravariant components labelled with an upper suffix. The above equation is rewritten in terms of Cartesian components as

$$X_{\alpha s} - X_{1s} = q^1 (X_{2s} - X_{1s}) + q^2 (X_{3s} - X_{1s}) + q^3 (X_{4s} - X_{1s})$$

which amount to three additional linear constraint relations for each atom not included in the minimal set, with a total number of $3(N - 4)$ equations defining a square matrix, of the same dimensionality, which must be inverted at the beginning of the simulation according to the procedure of Ref. [3]. Besides six Lagrange multipliers, associated with the distances among the first four atoms, are iteratively calculated and require the inversion of a 6×6 matrix at each time step. The linear constraint method thus introduces a total of $3N - 6$ constraints and an equal number of Lagrange multipliers which enter in the Cartesian equations of motion.

A second method [4] requires, for a completely rigid body, the definition of $3N - 6$ independent intramolecular distances and angles, R_n , whose displacements are constrained to vanish through the whole simulation. In practice the Cartesian coordinates are calculated with the simple position Verlet ignoring the kinematical restrictions and the subsequent introduction of constraints is a geometric problem, which is solved iteratively and does not involve forces, time step or Lagrange multipliers. Within each time step letting X_{is}^h be the constrained Cartesian coordinates accurate to the h th order, a better approximation,

accurate to the order $h + 1$, is given by Eq. (22) of Ref. [4] reported here as

$$X_{is}^{h+1} = X_{is}^h - \left(\frac{\partial X_{is}}{\partial R_n} \right)_\circ (R_n^h - R_n^\circ) \quad (1)$$

The labels $(^\circ)$ or (\circ) identify known quantities evaluated at the beginning of a time step and the value R_n^h , of the n th intramolecular parameter, is determined by the coordinates X_{is}^h , thus the differences $R_n^h - R_n^\circ$ vanish only up the h th order. The constant coefficients are given by

$$\left(\frac{\partial X_{is}}{\partial R_n} \right)_\circ = \frac{1}{m_i} g_{nm}^\circ \left(\frac{\partial R_m}{\partial X_{is}} \right)_\circ \quad \text{no sum over } i \quad (2)$$

and the quantities g_{nm}° form a matrix inverse to the Wilson's \mathbf{G} matrix [7] with elements

$$G_{nm} \equiv g_{\circ}^{nm} = \frac{1}{m_i} \left(\frac{\partial R_n}{\partial X_{is}} \right)_\circ \left(\frac{\partial R_m}{\partial X_{is}} \right)_\circ \quad (3)$$

where g_{nm}° and g_{\circ}^{nm} are covariant and contravariant components, respectively, of the metric tensor in the subspace of internal coordinates. These components do not depend on the Cartesian system used for their numerical evaluation therefore, for a rigid molecule, a $3N - 6$ square \mathbf{G} matrix is calculated and inverted only once, at the beginning of the simulation. From this point of view the procedure is similar to the method of linear constraints, which requires a single inversion of a $3(N - 4)$ square matrix and, in addition, the inversion of a 6×6 matrix at each time step. It will be however shown, in Section 5, that for a rigid molecule it is not necessary to define internal coordinates as it is sufficient to consider only translational and rotational variables.

A different method is based on the Euler equations of motion of a rigid body, usually implemented [8,9] in terms of quaternions as first proposed by Evans [10]. The equations of motion will not be discussed here and only the results are considered, obtained with an enhanced leap frog scheme [6], so called because the normalization of the four quaternions is not forced, as it is usually done, but dealt with through a Lagrange multiplier. Despite this improvement our calculations, reported in Section 6, show that the accuracy achieved with the enhanced leap frog is unsatisfactory and in any case lower than that provided by the methods of Refs. [3,4].

Quaternions were not used in Ref. [11] where the orientation of each body, in a system of rigid molecules, is specified by a 3×3 matrix under the constraint that it is orthogonal and represents a proper rotation. In this method six Lagrange multipliers are introduced, which form a symmetric 3×3 matrix and lead to a system of non-linear equations solved iteratively with an approximate Newton method. The iteration is avoided in a subsequent paper [5], which presents a symplectic splitting method for rigid bodies whose orientation is integrated through a sequence of planar rotations. The calculations of Section 6 confirm that this procedure is better than that based on quaternions, with conservation in time of the total energy practically identical with that obtained with

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