
Molecule-fixed axes in many-body Hamiltonians

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Résumé

The separation of the dynamics of the quantum many-body systems into the overall rotation and internal motions leads to their quantization in rotating frames. Whereas the rotating body frame is unique for a rigid body, there is a great degree of freedom for choosing a body frame for a general rotating and vibrating N-particle system. This, in turn, implies the need to study many-body systems for a class of body frames.

The concept of vibrational coordinates and of rotational coordinates is particularly clear for the case of a triatomic molecule: three particles form a single plane, in which the molecule vibrates, and at the same time the molecular plane rotates in the space-fixed frame of reference. The overall molecular rotation is made explicit by means of an orthogonal transformation, which brings the space-fixed into the body-fixed axes. The direction perpendicular to the molecular plane uniquely determines one of the three axes of the frame. Rotation about this direction will change the position of the axes in the molecular plane, in fact the axis system. It is already intuitively clear that this axis transformation will not affect the vibrational portion of the kinetic energy operator. The other parts of the kinetic energy, the rotational part and the rotation-vibration coupling part, will then need to adjust themselves to the new definition of the body frame. In this fashion, we may address the problem of the interaction of rotations and vibrations, which is one of the most important problems in molecular studies.

The variation of the rovibrational kinetic energy operator following a change of orientation of the axis system is investigated in the present work from the physical and mathematical points of view. Various types of axis embedding are analyzed in a systematic fashion for triatomic molecules of arbitrary structure, including the bisector, principal axis, and Eckart frames. We also consider the bisector axis embedding for tetratomic molecules and the local axis embedding for pentatomic molecules. Different axis conventions lead sometimes to a complex entanglement of rotational and vibrational motions, which may pose serious obstacles to numerically exact approaches.

Mots-Clés: kinetic energy operators, rotating frames

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