I. INTRODUCTION

Due to rapid progress in experiments with cold atom samples, there is an important need for modelization and theoretical interpretation. Numerical tools should be constantly refined for the treatment of atomic collisions at very low energy or for the determination of the bound vibrational levels of an alkali dimer close to the dissociation limit. Among the many applications, we may emphasize the following:

1. The determination of cross sections for fine-structure transitions or predissociation in a magneto-optical trap.
2. The population of vibrational levels of an excited electronic state by photoassociation of cold atoms (see, for instance, Refs. 5–7).
3. The study of long-lived cold molecule formation by spontaneous emission from the later state, as recently observed.†

Grid numerical methods using fast Fourier transform have proved to be very efficient for quantum molecular dynamics.§,‖ Wave functions are then represented on grids with a constant step in the momentum or coordinate spaces. However, their application to the present class of problems is not straightforward due to the coexistence of two regions of space with very different physical properties. There is a long-range region where the relative motion of the atoms is very slow, so that the de Broglie wavelength is very large, up to hundreds of atomic units \( a_0 = 0.052\,917\,72\,\text{nm} \). In contrast, in the inner region where chemical attractive forces become important, the kinetic energy is large so that the de Broglie wavelength is smaller than \( a_0 \). In the long-range region, the interaction potential is decreasing as \( R^{-\alpha} \), \( R \) being the internuclear distance: we shall focus on examples for which \( n = 3 \) — relevant to problems with dissociation limit \( \Lambda(n s) + \Lambda(n p) \), one alkali atom \( \Lambda \) being in the ground state, the other in the first excited state—and \( n = 6 \) — relevant to dissociation into \( \Lambda(n s) \).

As the maximum grid step in the position space is necessarily linked to the maximum momentum \( p_{\text{max}} \) considered in the physical problem, the choice of a constant grid step leads to the definition of a domain in the phase space with rectangular shape and area \( 2L \times p_{\text{max}} \), where \( L \) is the length of the grid in the position space. Therefore this rectangular domain is too extended in the long-range region, where only very small momenta should be included. In order to optimize the efficiency of the representation of the grid, Fattal et al.‖ have suggested a mapping procedure, a change of variable dealing for the dependence of the local wavelength with the distance. They give an application to the solution of the Schrödinger equation with a Coulomb potential. Our aim in the present paper is to extend their work to potentials asymptotically varying as \( R^{-\alpha} \), considering both one channel and multichannel applications.

For such potentials, a change of variable, already sug-
gested in the book of Landau and Lifshitz, has been used by O’Malley et al. for electron atom scattering and later on by Gribakin and Flambaum in their semiclassical treatment of cold collisions. Their aim was to obtain analytical solutions in the asymptotic region.

Change of variables for grid-based methods have been analyzed by Bayliss and Turkel and employed by Gygi or, more recently, by Pérez-Jordà for electronic structure calculations as well as by Tiesinga et al. for obtaining bound vibrational states of alkali dimers by a filter method. In the latter work, however, the emphasis is more on the filtering method to extract eigenvalues by means of the Green’s function approach. The formalism is applied to the many-channel problem of rovibrational levels coupled by hyperfine structure in the vicinity of the first excited asymptote of Na$_2$. In contrast, our goal in the present paper is to analyze in detail the implementation of a mapping procedure to improve the efficiency of grid method calculations for bound vibrational levels in the class of potentials described above. Starting with a one-channel problem, we shall compare the efficiency of an analytical change of variable, close to the one used in Ref. 18, with a purely numerical one. The accent will be put on the optimization of the phase space occupation, and on the definition of a symmetric representation of the Hamiltonian on the grid convenient for numerical accuracy. Indeed, Tuvi et al. have pointed out that a simple change of variables results in non-Hermitian Hamiltonian representation and suggested a way to symmetrize. We shall propose another procedure, better adapted to coupled channels with $d/dR$ radial coupling. Section II is devoted to the description of the mapping procedure, particularly in the case of $R^{-3}$ asymptotic potentials, with an estimation of the occupation of the phase space. In the two following sections we describe applications to the calculation of bound vibrational states, close to the dissociation limit, for examples relevant to photoassociation studies. In Sec. III, we have considered two cases of a potential, respectively, to the $^4\Sigma_g^+$ and $^1\Pi_g$ excited state of Na$_2$, and the $^1\Pi_u(6s + 6p^2P_{1/2})$ excited state of Cs$_2$. Indeed, the spectroscopy of those dimers can be interpreted using Hund’s case a representation for Na$_2$ and Hund’s case c for Cs$_2$. In contrast, Sec. V is devoted to the study of perturbations in Rb$_2$ fluorescence spectrum, considering two perturbations $^5\Sigma_g^+(5s + 5p^2P_{1/2})$ and $^5\Sigma_u^+(5s + 5p^2P_{3/2})$

Atomic units will be used except when otherwise stated.

II. MAPPED FOURIER GRID METHOD

A. Mapping procedure

In order to compute bound vibrational states of a diatomic molecule, a method, originally proposed in Refs. 9 and 20, was further developed by Monnerville and Robbe and by Dulieu et al. Let us recall briefly the principle of this method, hereafter referred to as Fourier Grid Method (FGM): the radial Schrödinger equation for eigenvalues problem is written as

$$[\mathbf{T} + \mathbf{V}(R)]\psi(R) = E\psi(R).$$  \hspace{1cm} (2.1)

A grid of $N$ points equally spaced over coordinate $R$ is defined as $R_i$, $(i=1,N)$. We introduce a set of functions defined at the grid points:

$$\varphi_i(R_j) = \delta(R_i - R_j) \quad (i,j=1,N).$$  \hspace{1cm} (2.2)

In this basis, both $\mathbf{T}$ and $\mathbf{V}(R)$ are represented by $N \times N$ matrices. The potential operator $\mathbf{V}(R)$ is diagonal in this representation, while the kinetic energy $\mathbf{T}$ is diagonal in the momentum representation, which is connected by a Fourier transform to the coordinate representation. Using well-known properties of the Fourier transform, the elements of the operator $\mathbf{T}$ can be written explicitly as a function of the number of points $N$—assumed to be even—and total length $L$ of the grid:

$$T_{i,i} = \frac{\pi^2 N^2 + 2}{\mu L^2}.$$  \hspace{1cm} (2.3)

$$T_{i,j} = (-1)^{i-j} \frac{\pi^2}{\mu L^2} \sin \left( (i-j) \pi/N \right).$$  \hspace{1cm} (2.4)

In Eqs. (2.3) and (2.4), $\mu$ is the reduced mass of the system. Eigenvalues $E_i$ are obtained by diagonalization of the $N \times N$ matrix $\mathbf{T} + \mathbf{V}$.

It is important to note that for the vibrational levels considered, the energy is close to the asymptotic value of the potential, hereafter taken as the energy origin. The maximum kinetic energy in the problem can be estimated by the depth $(V_{\text{max}} - V_{\text{min}})$ of the potential well. In most applications $V_{\text{max}} > V_{\text{min}}$, nonzero positive values corresponding to situations where the potential has a hump. For a grid of length $L$, the two-dimensional phase space should occupy at least a rectangular-shaped area:

$$A \geq L p_{\text{max}},$$  \hspace{1cm} (2.5)

where $p_{\text{max}}$ is the maximum momentum that has to be considered, corresponding to the maximum value of the kinetic energy:

$$p_{\text{max}} = \sqrt{2 \mu (V_{\text{max}} - V_{\text{min}})}.$$  \hspace{1cm} (2.6)

In practice, for a grid with $N$ points, with a constant grid step $\Delta R = L/N$, the Fourier method considers a momentum domain extending from $-p_{\text{grid}}$ to $+p_{\text{grid}}$ so that the phase space is a rectangle with area:

$$A_{\text{N}} = 2\pi N \hbar = 2 L p_{\text{grid}}.$$  \hspace{1cm} (2.7)

where, using atomic units, $\hbar = 1$. Therefore the constant grid step should verify

$$\Delta R = \frac{\pi}{p_{\text{grid}}} \leq \frac{\pi}{\sqrt{2 \mu (V_{\text{max}} - V_{\text{min}})}}.$$  \hspace{1cm} (2.8)

When the vibrational motion extends at very long range, the length $L$ has to be very large and calculations involve diagonalization of huge matrices $\mathbf{H} = \mathbf{T} + \mathbf{V}$. In fact, the grid contains too many points in the asymptotic region: indeed, at each distance $R$, the grid step needs only to be small enough to represent correctly the local kinetic energy. It is then sufficient to consider a local grid step $s(R)$ satisfying the condition
For the class of problems that we are considering (see Sec. III) the computation effort of the diagonalization procedures scales as the cube of the number of grid points. We propose to apply coordinate transformation in order to ‘‘compress’’ the grid at large distances. To that purpose, we define a transformation function \( g(R) \) to set a working grid \( x_i = g(R_i) \), with a constant step \( \Delta x \) related to the variable step in the physical grid through

\[
s(R) = \frac{\Delta x}{g'(R)}. \tag{2.10}
\]

The transformation function is obtained, by comparing Eqs. (2.10) and (2.9) as

\[
x = g(R) = \int_{R_0}^{R} \frac{\sqrt{2\mu[V_{\text{max}} - V(r)]]}}{\pi} \, dr. \tag{2.11}
\]

It is easy to check that in the working grid the minimum step is

\[
\Delta x = 1. \tag{2.12}
\]

In Eq. (2.11), the integration domain starts at a distance \( R_0 \) slightly smaller than the position of the repulsive potential wall at short range. Now the physical grid is well adapted to different regions of the potential, since in the asymptotic region the local step \( s(R) \) becomes much larger than at short internuclear distances. In Fig. 1, we have illustrated this behavior considering various potentials for Na\(_2\)\(^{24} \) or Cs\(_2\)\(^{25} \) with either \( R^{-3} \) or \( R^{-6} \) asymptotic behavior. For a constant step \( \Delta x = 1 \) in the working grid, we have represented in Fig. 2 the variation of \( s(R) \) as a function of the distance \( R \). The marked dependence upon the value of the \( n \) exponent manifests itself clearly, the step \( s(R) \) increasing more rapidly with the distance in case of a \( R^{-6} \) potential. Besides, due to the mass factor present in Eq. (2.9) the \( R \) variation is more rapid for Na\(_2\) than for Cs\(_2\). These features, as well as the role of the position \( R_0 \) of the inner repulsive potential wall, will be discussed more explicitly in Sec. II C.

Alternatively, in Eq. (2.9) defining a maximum local grid step, the real potential \( V(R) \) can be replaced by another potential \( V_{\text{env}}(R) \), provided the local kinetic energy stays larger than or equal to the real one. We shall call \( V_{\text{env}}(R) \) an ‘‘enveloping potential’’ as the corresponding potential curve lies below the real one. The local grid step is now such that

\[
s_{\text{env}}(R) = \frac{\pi}{\sqrt{2\mu[V_{\text{max}} - V_{\text{env}}(R)]} \leq s(R). \tag{2.13}
\]

Therefore the number of points on the grid is necessarily increased compared to the previous one. We discuss in Sec. II C examples where the asymptotic expression of the potential is considered.

Finally, for the discussion of the convergence of the calculations, it is convenient to introduce an auxiliary parameter \( \beta_R = s_{\text{env}}(R)/s(R) \). If the enveloping potential differs from the real one, \( \beta_R \) depends upon \( R \), with the restriction \( \beta_R \leq 1 \) so that the number of grid points is sufficient. Moreover, we can, starting from the real potential, calculate \( s(R) \), and choose a constant \( \beta < 1 \) (for instance, the minimum value of \( \beta_R \)) in order to define a local grid step such that \( s_{\beta}(R) = \beta s(R) \). It means that the density of points is \( 1/\beta \) times larger than the critical density defined by (2.12), the step in the working grid being now

\[
\Delta x = \beta, \tag{2.14}
\]

corresponding in the physical grid to a larger extension of the momentum, from \(-p_{\text{grid}} \leq p_{\text{grid}} \leq p_{\text{max}} / \beta\).

**B. Transformation of the Hamiltonian**

Changing in the Schrödinger equation

\[
-\frac{1}{2\mu} \frac{d^2}{dR^2} \psi + V(R) \psi = E \psi, \tag{2.15}
\]

the variable \( R \) into another \( x \) with the transformation
\[ R = f(x), \quad dR = J(x)dx, \quad J(x) = f'(x), \] (2.16)

one gets

\[ \left( -\frac{1}{2\mu J^2} \frac{d^2}{dx^2} + \frac{J'}{2\mu J} \frac{d}{dx} + V(x) \right) \psi = E \psi, \] (2.17)

where \( J' = dJ/dx \). As discussed in the Appendix, the elements \( T_{ij} \) and \( T_{ji} \) of the kinetic energy operator in the FGH representation are generally different, leading to the diagonalization of a nonsymmetric matrix.

In order to introduce a Hamiltonian matrix symmetric in the FGH representation, we define a new wave function \( \phi(x) \):

\[ \psi(x) = J^{-1/2}(x) \phi(x), \] (2.18)

so that the Eq. (2.17) becomes

\[ \left( -\frac{1}{2\mu J^2} \frac{d^2}{dx^2} + \frac{J'}{2\mu J} \frac{d}{dx} + V + \frac{1}{2\mu} \left( -\frac{5}{4} \left( J' \right)^2 + \frac{1}{2} J'' \right) \right) \times \phi(x) = E \phi(x). \] (2.19)

We can rewrite this equation in a symmetrical form as

\[ \left( -\frac{1}{4\mu} \frac{d^2}{dx^2} + \frac{d}{dx} + V \right) \phi = E \phi, \] (2.20)

where we have introduced an effective potential by

\[ V_{\text{eff}}(x) = V(x) + \frac{1}{2\mu} \left( \frac{7}{4} \left( J' \right)^2 - \frac{1}{2} J'' \right). \] (2.21)

We can check that the indexes \( i \) and \( j \) now play the same role in the expression of the kinetic operator \( T \) matrix elements:

\[ T_{ij} = (-1)^{i-j} \frac{\pi^2}{2\mu J^2} \frac{1}{\sin^2[(i-j)/N]} \left( \frac{1}{J_i^2} + \frac{1}{J_j^2} \right), \] (2.22)

if \( i \neq j \), while

\[ T_{ii} = \frac{\pi^2}{\mu L} \left( N^2 + 2 \right) \frac{1}{J_i^2}. \] (2.23)

As a consequence, the FGH representation yields a symmetrical Hamiltonian matrix, so that efficient diagonalization procedures designed for triangular matrices can be implemented.

C. Mapping using \( R^{-3} \) and \( R^{-6} \) analytical potentials and a repulsive wall

In the derivation of the mapping procedure, we can use as an “enveloping potential” in Eq. (2.13) any analytic potential \( V_{\text{env}}(R) = -C_{\text{env}}/R^n \), such that the corresponding potential curve lies below \( V(R) \).

The Schrödinger equation for a potential with \( R^{-n} \) behavior, \( n \) being an integer value such that \( n \geq 3 \), was discussed by many authors: in Refs. 12–14, a change of variable is introduced in order to transform the Schrödinger equation into the Bessel equation for which analytical solutions can be found. In the present approach, performing integration of the right-hand side of Eq. (2.11), we obtain:

\[
\begin{align*}
R &= f(x), \\
dR &= J(x)dx, \\
J(x) &= f'(x), \\
\frac{d^2}{dx^2} + \frac{J'}{2\mu J} \frac{d}{dx} + V &= E. 
\end{align*}
\] (2.16)

One gets

\[
\left( -\frac{1}{2\mu J^2} \frac{d^2}{dx^2} + \frac{J'}{2\mu J} \frac{d}{dx} + V + \frac{1}{2\mu} \left( -\frac{5}{4} \left( J' \right)^2 + \frac{1}{2} J'' \right) \right) \times \phi(x) = E \phi(x). 
\] (2.17)

Whereas the physical grid is extending from \( R_0 \) (chosen at a distance shorter than the position of the repulsive wall of the actual potential) to \( R_{\max} \), the new grid is varying from 0 to a maximum value that is limited by the finite value \( x_{0,n} \), depending both on the asymptotic behavior of the potential (through \( \alpha_n \) and \( n \)) and on \( R_0 \). There is therefore an accumulation of points in the vicinity of \( x_{0,n} \), which is never explicitly reached. At small distances, due to the existence of a repulsive wall in our potential, we do not encounter the problem of the accumulation of points at the origin that had to be considered in Ref. 11 for the Coulomb problem.

The relation between the constant step \( \Delta x \) on the working grid and the variable step \( s_n(R) \) on the physical grid is readily obtained as

\[
s_n(R) = \frac{R^{n/2}}{\alpha_n} \Delta x. 
\] (2.27)

The role of the exponent \( n \) and of the mass factor in \( \alpha_n \) appears clearly in Eq. (2.27) and has been illustrated in Fig. 2. We also display as an example in Fig. 3, in a case where \( n = 3 \), corresponding to the asymptotic behavior of the upper attractive \( 1 \) curve of Cs\(_2\), the repartition of the grid points for the working grid and for the physical grid: the adaptive character of the mapping procedure is demonstrated by the fewer number of points in the working grid when the internuclear distance is increasing. In the case of potential \(-C_{\text{env}}/R^3\), the change of variable should be

\[
x_4 = x_{0,3} - 2 \alpha_3 R^{-1/2}; 
\] (2.28)
where we have defined \( \alpha_3 = \sqrt{2 \mu C_3^{env} / \pi} \) through Eq. (2.25). The inverse transformation is then analytical:

\[
R = f_3(x_3) = \frac{(2 \alpha_3)^2}{(x_{0,3} - x_3)^2}.
\] (2.29)

As the change of function described in Sec. II B differs from what was proposed in the references quoted above,\(^{12-14}\) our new Schrödinger equation differs from a Bessel equation, and it is more convenient for numerical calculations, as it leads to symmetrical matrices in the FGH representation:

\[
\left[ - \frac{1}{2\mu} \left( \frac{(x_{0,3} - x_3)^6}{2'(\alpha_3)^4} \frac{d^2}{dx_3^2} + \frac{d^2}{dx_3^2} \frac{(x_{0,3} - x_3)^6}{2'(\alpha_3)^4} \right) + \bar{V}(x_3) \right] \times \phi(x_3) = E \phi(x_3),
\] (2.30)

with new potential \( \bar{V} \):

\[
\bar{V}(x_3) = V(x_3) + \frac{1}{2\mu} \frac{39}{2^8(\alpha_3)^4} (x_{0,3} - x_3)^4.
\] (2.31)

In the new coordinate \( x_3 \), the asymptotic behavior of \( V(x_3) \) obtained by the transformation of \(- C_3^3/R^3\) is

\[
V_{as}(x) = -\frac{1}{2\mu} \frac{4\pi^2}{2^8(\alpha_3)^4} (x_{0,3} - x_3)^6,
\] (2.32)

so that when \( C_3^{env} = C_3 \), the effective potential, in the asymptotic region, may be written:

\[
\bar{V}_{as}(x_3) = \frac{1}{2\mu} \left( -\frac{4\pi^2}{2^8(\alpha_3)^4} (x_{0,3} - x_3)^6 \right.
\]

\[
\left. + \frac{39}{2^8(\alpha_3)^4} (x_{0,3} - x_3)^4 \right).
\] (2.33)

The matrix elements for the kinetic energy operator are now

\[
T_{ij} = (-1)^{i-j} \frac{\pi^2}{2\mu L^2} \frac{1}{\sin^2[(i-j)\pi/N]} \times \left( \frac{(x_{0,3} - x_{3,j})^6}{2'(\alpha_3)^4} + \frac{(x_{0,3} - x_{3,i})^6}{2'(\alpha_3)^4} \right),
\] (2.34)

if \( i \neq j \), while

\[
T_{ii} = \frac{\pi^2}{\mu L^2} \frac{N^2 + 2}{6} (x_{0,3} - x_{3,i})^6.
\] (2.35)

D. Comparison of the numerical and the analytical mapping procedures

The analytic approach enables a simple assessment of the procedure. However, the computing code has to be modified for potentials differing in their asymptotic expression, which is not the case for the general numerical procedure.

Another disadvantage of the analytical approach lies in the definition of an enveloping potential. In many cases, due to the existence of higher-order attractive terms in the multipole expansion, the asymptotic curve \(- C_3^3/R^3\) crosses the \( V(R) \) curve. Therefore, the value of \( C_3^{env} \) should be chosen much larger than the actual \( C_3 \) value. For example, as illustrated in Fig. 4, the asymptotic behavior of \( \text{Na}_2^3 \Pi_u(3s + 3p^2 P) \) is \(-6.48/30\), but only the enveloping curve with \( C_3^{env} = 18.0 \) lies under \( V(R) \) for all internuclear distances. In the latter case, the use of an enveloping analytical potential in Eq. (2.13) results in a number of grid points four times larger than when the real potential is used in Eq. (2.11). This drawback is particularly important for cases corresponding to small values of \( R_p \), the divergence of \( C_3^3/R^3 \) near the origin resulting in a significant increase of the number of grid points \( N \). Moreover, increasing the phase space of the problem when using small grid steps near the origin may lead to spurious eigenvalues in the numerical diagonalization procedure. It also increases significantly the spectral range of the Hamiltonian operator. This will hinder the use of direct propagation methods.

It seems therefore more convenient to use the real potential in Eq. (2.11). The mapping transformation is calculated for any potential, irrespective of its asymptotic behavior. The integral in Eq. (2.11) and all derivatives of \( g(R) \) are then obtained through purely numerical procedures.

E. Occupation of the phase space domain after coordinate transformation

As discussed by Fattal et al.,\(^{11}\) and by Kosloff,\(^{10}\) mapping procedures are capable of optimizing the use of the phase space volume of the representation. As a first approximation, the phase space domain necessary to describe the system can be estimated by considering the classical trajectory corresponding to the highest vibrational level that we want to compute. This is illustrated in Fig. 5, where we have drawn the phase domain in distance \( R \) and momentum \( p \) spanned by a classical trajectory corresponding to a vibrational motion with binding energy \( 1.3 \times 10^{-7} \), i.e., \( E_p = -0.295 \text{ cm}^{-1} \), in the potential \( C_3^3(1_s) \) displayed in Figs. 1 and 2. The shape differs markedly from rectangular, showing that at large distances, due to the very small value of the local momentum, only a very small part of the phase space defined by a grid with a constant grid step is occupied.

The same domain in the new variables \( x \) and \( P_x \) is presented also. In the working grid, the variable \( x \) is defined in
The numerical treatment should therefore involve at least \( N \) grid points. After mapping with enveloping potential, the area spanned by the grid is defined as \( A_{3}^{\text{mapp}} \approx 2x_{3,\text{max}}P_{3,\text{max}} \), so that in the chosen example we have \( A_{3}^{\text{mapp}} \approx 1705 \approx 2 \pi \times 272 \), so that the minimum number of grid points is reduced to 272. Finally, when the mapping procedure based on the real potential, the area \( A_{3}^{\text{mapp}} \approx 2x_{3,\text{max}}P_{3,\text{max}} \) now is at least 1077, corresponding to a minimum number of grid points of 172 only, very close to the number \( N_{c} = 165 \) of cells estimated from the classical phase space restricted to the same energy. The efficiency of the numerical mapping method is therefore clearly demonstrated by this figure.

One should note that this approach to the estimation of phase space confined by the problem is completely classical. It assumes that the quantum density in phase space decays exponentially fast in the classical forbidden region. The definition of the phase space in quantum mechanics was done by Hillery et al. in Ref. 28. Using the Wigner distribution function, the exponential decay of the quantum density outside the classical allowed region is clearly evident. If tunneling is important, the phase space region involved, both in coordinate and momentum has to be included in the grid, so that a larger number of grid points should be considered. The introduction of a parameter \( \beta \) as defined in Eq. (2.14), in order to reduce the step in the working grid is then justified, and this parameter needs to be optimized in the calculations. We describe some examples below.

### III. APPLICATION TO THE CALCULATION OF BOUND VIBRATIONAL LEVELS FOR A SINGLE LONG-RANGE POTENTIAL: EXAMPLES FOR Na\(_2\) AND Cs\(_2\)

The efficiency and accuracy of the mapped FGH method described above can be checked by comparison with a standard method, such as the well-known Numerov Cooley algorithm, as well as with the usual Numerov method.

As discussed in the Introduction, we have chosen two potentials relevant to implementation of spectroscopy experiments, and corresponding to Hund’s case \( a \) representation for \( \text{Na}_2 \) and Hund’s case \( c \) for \( \text{Cs}_2 \). We have performed accuracy tests computing the energies of the first 80 vibrational levels in the potential \( \text{Na}_2 \Pi_2^0(3s + 3p^2 P) \) already displayed in Fig. 1 extended at long range by the asymptotic \(-6.48/R^3 \) curve predicted in Ref. 26. We chose a grid extending from 5.0\( a_0 \) to 90\( a_0 \), and we display in Fig. 6 the results of the convergence tests. The precision of the Numerov method itself is illustrated in the upper panel, where we show that the computed vibrational energies \( E_v \) vary by less than \( 4 \times 10^{-3} \text{ cm}^{-1} \) when the step size is modified from \( \Delta R = 0.00125a_0 \) (68,000 points) to \( \Delta R = 0.0025a_0 \) (34,000 points). The binding energies extend from 1103.78 to 2.44 \text{ cm}^{-1} \). Taking as a reference the first calculations with the Numerov algorithm, we show that a typical \( 10^{-5} \text{ cm}^{-1} \) accuracy can be obtained with the FGH method using a constant step and a number of points of the order of 1000.

The convergence tests for the mapped FGH method varying the \( \beta \) parameter are also given in the figure. The same level of accuracy can be reached with \( \beta = 0.2 \) and \( N = 506 \) grid points, thus reducing \( N \) by a factor of 2. We should note that the accuracy obtained with \( \beta = 0.6 \) is already

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**FIG. 5.** Solid lines: The classical energy shell in phase space with and without the coordinate transformation, for the vibrational level with binding energy \( E_v = -0.295 \text{ cm}^{-1} \) in the attractive potential \( C_{5s}(1.6s + 6p^2 P y_2) \). (a) The main figure shows the energy shell in phase space without any mapping. (b) The upper inset displays the energy shell with the mapping defined by the enveloping potential \(-C_{5s}^{\text{env}}/R^3\) with \( C_{5s}^{\text{env}} = 24.42\). The lower inset displays the energy shell in phase space with the mapping using the real behavior of the potential. The area \( S = 1034 \text{ a.u.} \) defined by the contour is the same for all three cases. The number of phase cells \( N_c \) is connected with \( S \) through \( S = 2 \pi \times N_c \). Broken lines: The rectangles defining the phase space used in the calculations. One can see that without the mapping a larger phase volume is used in the calculation, that requires proportionally more grid points. The third case is most efficient in that sense.
better than $10^{-3}\text{cm}^{-1}$, and corresponds only to 170 grid points for the determination of 80 vibrational levels. In contrast, for $\beta=1$, only the 20 lowest levels are obtained accurately, the error on the energy of levels $\nu \geq 40$ reaching 0.5 cm$^{-1}$. Finally, we have checked that for $\beta>1$, the method is not even yielding all the eigenenergies.

The calculated error on the energy resulting from the Numerov calculation (Fig. 6) is clearly nonuniform. Indeed, changing the number of grid points modifies the local description of the potential curve, which will affect mainly energy levels with outer turning points located in the region $10\alpha_0 < R < 16\alpha_0$, where the slope of the potential is large. In contrast, the calculated error in the FGH method is uniformly distributed on all levels, due to the global character of the method.

The latter example is not intended to check the efficiency of the mapping procedure, as the vibrational motion extends only to $90\alpha_0$. Considering now the example of the $1_g (6s + 6p^2P_{3/2})$ potential of Cs$_2$, we have computed the vibrational levels up to $\nu = 337$, with a grid extending from $4.5\alpha_0$ to $500\alpha_0$. The number of points can be reduced from 6500, without a coordinate change, to 658 with the simple transformation defined in Eq. (2.11), using a value $\beta=0.6$ reducing the memory necessary for computation by a factor 120. For the chosen example, the highest calculated vibrational level has an energy as small as $E_{337} = -0.0317\text{cm}^{-1}$, the $\nu=0$ level staying at $E_0 = -1359.6804\text{cm}^{-1}$. The convergence tests show a stability better than $10^{-4}\text{cm}^{-1}$, when the parameter $\beta$ is varied from 0.9 to 0.4. The diagonalization procedure yields $N$ eigenvalues, for which only the lower ones correspond to bound states, the upper ones being continuum states up to a positive energy $E_{\beta \text{max}}$ that depends upon $\beta$. The efficiency of the mapping using the real potential is clearly manifested in this example: for the grid considered above, choosing $\beta=0.6$, mapping using the real potential involve 658 grid points and hence 658 eigenvalues, the upper one lying at an energy $E_{\beta \text{max}} = 12729\text{cm}^{-1}$. The same calculations with an enveloping potential $-C_3/R^3$ (where we have taken $C_3^{\text{env}} = C_3$ so that the enveloping curve differs from the real one only at short and intermediate distances), would require $N = 878$ grid points. The increase in the number of points is not a substantial one, but the maximum energy is now $E_{\beta \text{max}} = 87790\text{cm}^{-1}$, so that the energy domain spanned by the method is as high as $89000\text{cm}^{-1}$. Such a large energy range can result into a severe inconvenience for the calculation to time-dependent problems.

The repartition of grid points in the example has been illustrated in Fig. 3. It is remarkable that vibrational energies can be obtained with accuracy better than $10^{-4}\text{cm}^{-1}$ using only $N = 564$ grid points (with $\beta=0.9$) for levels with a wave function exhibiting up to 337 nodes. A possible drawback of this achievement could be that $N$ becomes too small for an accurate definition of the wave function: we show below that this is not the case.

**IV. THE WAVE FUNCTION IN THE FGH METHOD**

In calculations employing a discrete grid, the wave function is represented on a finite set of grid points. Values of the wave function at other distances have therefore to be determined by interpolation. Linear interpolation then yields low-

![FIG. 6. Accuracy $\Delta E$ of the computed energies for the 80 lowest vibrational levels in the $^1\Pi_g (3s + 3p)$ potential of Na$_2$ represented in Fig. 1. The vibrational number $\nu$ is indicated on the horizontal axis. The uppermost level considered has $2.34\text{cm}^{-1}$ binding energy. The physical grid is extending from $5\alpha_0$ to $90\alpha_0$. As reference values, we consider energies computed through a Numerov integration on a grid with step $\Delta R = 0.00125\alpha_0$ (68 000 points). The three figures represent (a) $\Delta E$, from Numerov integration with $\Delta R = 0.0025\alpha_0$ (34 000 points); (b) $\Delta E$, for energies computed by the FGH method with a uniform grid. Solid line: $N = 950$ points; dash–dotted line: $N = 1140$ points; (c) $\Delta E$, for the FGH method with the mapping defined by Eq. (2.11), considering different values of the parameter $\beta$. Solid line: $\beta = 0.6$, $N = 170$ points; dash–dotted line: $\beta = 0.4$, $N = 254$ points; dashed line: $\beta = 0.2$, $N = 506$ points.](image1)

![FIG. 7. The $\nu = 332$ vibrational wave function for the $1_g (6s + 6p^2P_{3/2})$ potential of Cs$_2$ (see Fig. 1), computed at the grid points defined with the mapping of Eq. (2.11). Here, $R_{\text{max}} = 500\alpha_0$, $N = 564$. (a) The wave function at every grid point, with linear interpolation between two points; (b) the wave function interpolated according to Eq. (4.1) choosing $N_{\text{map}} = 10 000$ (see the text). (c) The Interpolated wave function in the $x$ variable, showing only the part corresponding to large $R$. Comparing (c) to (b), one can appreciate the regularity of the oscillations in the mapped wave function.](image2)
quality results (see Fig. 7). Here we describe a better approach for the interpolation of the wave function in the FGH method, using the intrinsic properties of the Fourier representation.\textsuperscript{10}

The interpolated wave function in this case is\textsuperscript{10}
\[
\psi(q) = \sum_{j=1}^{N} \psi(q_j) \text{sinc} \left( \frac{\pi}{\Delta q} (q - q_j) \right),
\]
where \(q_j\) is a grid node (with or without mapping), \(q\) is any intermediate point, \(\Delta q\) is a grid step, and we have defined the function \(\text{sinc}(z) = \sin(z)/z\). In Fig. 7, we display the wave function, computed with sinc interpolation at a large number (\(N_{\text{interp}} = 10,000\)) of \(q\) values, for the 333rd \((v = 332)\) vibrational level of Cs\(_2\)(1\(g\)). A comparison with linear interpolation clearly illustrates the good quality of the second interpolation. Of course, we have checked the accuracy of the interpolated wave functions by comparing to standard methods.

In the same figure, we show the influence of the mapping procedure on the shape of the wave function. One can see that the two representations are quite different: the mapping has an effect of "stretching" the grid at smaller distances, where the density of points needs to be large. Indeed, if the unmapped grid has sufficient point density in this region, it has too many points at large distances, where oscillations of the wave function are not so frequent. The mapping procedure eliminates such superfluous points, yielding a uniform distribution of the number of grid points per oscillation. It is remarkable that with mapping, good quality wave functions can be obtained with a reduced number of points at each oscillation: indeed, the wave function drawn in Fig. 7 has 332 nodes and has been obtained using only \(N = 564\) grid points, which is less than two points per oscillation.

V. EXAMPLE OF TWO COUPLED STATES: PERTURBATIONS IN RB\(_2\) SPECTRUM

The mapped Fourier Grid Hamiltonian method presented in the previous section can easily be generalized to calculate the energies of the rovibrational levels considering several coupled molecular electronic states. We have shown previously\textsuperscript{7} that the FGH approach is particularly well suited for such a goal, compared to more traditional approaches like Numerov integration methods. We describe here below calculations considering two coupled states in a diabatic representation. The implementation of the calculation from the previous section is straightforward, provided the same mapping procedure is applied to both channels. For a grid of \(N\) points, we now consider three operators \(T\), \(V(R)\), and \(W(R)\), each represented by a \(2N \times 2N\) square matrix as follows:
\[
T = \begin{pmatrix} T_1 & 0 \\ 0 & T_2 \end{pmatrix} \quad V = \begin{pmatrix} V_1 & 0 \\ 0 & V_2 \end{pmatrix} \quad W = \begin{pmatrix} W_1 & W_{12} \\ W_{12} & W_2 \end{pmatrix}.
\]

The kinetic energy matrix \(T\) is block diagonal, each block deduced from Eqs. (2.22) and (2.23). The potential energy matrix \(V(R)\) is diagonal in the FGH representation: each diagonal block \(V_1\) and \(V_2\) should contain the mapping of the corresponding potential energy curve. In contrast, in a diabatic representation, the coupling matrix \(W(R)\) contains both diagonal \((W_1, W_2)\) and nondiagonal \((W_{12} \text{ and } W_{21})\) blocks terms. Obviously, this procedure may be generalized to any number of coupled electronic states. The diagonalization of the full matrix provides the energies of the levels of the coupled system. The problem is to generalize the mapping procedure: this can be done by considering an enveloping potential adapted to the two different potentials and eventually to the coupling term.

As an example, we use this method for the calculation of the bound vibrational levels of the \(A^1\Sigma_g^+ (0^+_v)\) and the \(b^3\Pi_u (0^+_v)\) excited electronic states in Rb\(_2\), coupled by spin–orbit interaction. Both states are behaving asymptotically as \(R^{-3}\), and are correlated to the first excited dissociation limit \(5s + 5p\). It is well known that, due to the spin–orbit coupling between those two states, perturbations\textsuperscript{30} are observed in the spectra of all alkali dimer molecules: many theoretical and experimental studies have been performed for Li\(_2\),\textsuperscript{31–34} Na\(_2\),\textsuperscript{35,36} K\(_2\),\textsuperscript{37} Cs\(_2\),\textsuperscript{38} while only a single low resolution experiment has investigated this interaction in Rb\(_2\).\textsuperscript{39}

In the present work, the Rb\(_2\) potential curves are taken from the accurate \textit{ab initio} pseudopotential calculations of Fourcraut et al.,\textsuperscript{40} matched to the asymptotic curves of Ref. 26. The spin–orbit effective operator is assumed to be \(R\) independent and proportional to the atomic fine structure splitting \(\Delta E_\text{fs}\). The coupling term is then \(W_{12} = \Delta E_\text{fs}(\sqrt{2}/3)\), while the energy of the \(b^3\Pi_u\) electronic state is corrected by \(W_2 = -\Delta E_\text{fs}/3\), shifting down its dissociation limit. The mapping function is deduced from Eq. (2.13), using for the enveloping potential,
\[
V^\text{env}(R) = \inf[V_1(R), V_2(R)], \quad R > \inf(R_{e1}, R_{e2}),
\]  
\[
V^\text{env}(R) = \inf[V_1(R_{e1}), V_2(R_{e2})], \quad R < \inf(R_{e1}, R_{e2}),
\]

where \(R_{e1}\) and \(R_{e2}\) are the positions of the minima of the potential curves \(V_1(R)\) and \(V_2(R)\), respectively, while \(\inf(a, b)\) means the lower of the two numbers. The potential curves are drawn in Fig. 8 in Hund’s case \(a\) (\(A^1\Sigma_g^+\) and \(b^3\Pi_u\) states) and Hund’s case \(c\) \([0^+_v (5s + 5p^2P_{1(2,32)})\) states representations. Two aspects need to be discussed in the choice of the enveloping potential in this two-channel problem: first the dissociation limit is now an important issue, as it may introduce significant local kinetic energy. Taking the Hund’s case \(c\) lower potential curve as an enveloping potential would increase the local kinetic energy, all over the grid, by \(2\Delta E_\text{fs}/3 = 158.4.20\) cm\(^{-1}\). The introduction of a \(B\) factor is increasing the momentum domain to address this issue. Second, in contrast with the previous discussion, we have taken the enveloping curve as constant from the position of the first grid point to the distance of the potential minimum: this introduces only a few (around 20) additional grid points, but from numerical point of view it simplifies markedly the situation in the region of small internuclear distances \(R\), where the real potential is rapidly varying as a function of \(R\).
mixing between the two channels, as many \( B_v \) values are not lying on any of the four preceding curves. Besides, strong perturbations are found, manifested by oscillations in the computed constants. In contrast with lighter alkali dimers like \( \text{Li}_2, \text{Na}_2, \text{K}_2 \), we predict that the whole spectra is concerned by these perturbations, and can be described neither in the framework of the Hund’s case \( a \) nor Hund’s case \( c \) independent channel representation. In a standard spectroscopy experiment, one may expect strong irregularities in the observed spectra, making a full identification very difficult.

An example of the irregularities predicted by the present calculations is analyzed in more details in Fig. 10, where we have represented the variation of the rotational constant in the vicinity of the \( D_1 \) dissociation limit. Let us note that the mapping represents a crucial improvement to obtain accurate results in this energy range. The oscillatory behavior of \( B_v \) shows that the Hund’s case \( c \) picture is adapted only to a few levels that we may assign to the lower electronic state \( 0^+_u (D_1) \), most of the others being perturbed. When the \( B_v \) value is minimum, the corresponding wave function is indeed very close to unperturbed vibrational motion in the single channel \( 0^+_u (D_1) \), as is illustrated in Fig. 11. In contrast, the maxima of the oscillations correspond to an important admixture of a \( 0^+_u (D_2) \) wave function, where the vibrational motion is confined at shorter distances, with an outer turning point that in the example chosen for the figure is close to \( 22a_0 \) instead of \( 50a_0 \). Preliminary experimental results\(^{41}\) seem to confirm this oscillatory behavior of the rotational constant.

Above the \( D_1 \) dissociation limit, the coupling between the two channels is also responsible for the predissociation of the \( 0^+_u (D_2) \) bound levels into a continuum of two \( nS^2S_{1/2} \) and \( np^2P_{1/2} \) free atoms. This process has been recently investigated as a detection tool of \( K_2 \) molecules in a photoassociation experiment\(^{42}\) and could be extended to \( \text{Rb}_2 \), since the broadening of the \( 0^+_u \) lines in \( \text{Rb}_2 \) photoassociation spectra has already been reported.\(^{43}\)

In the present calculations we find that a similar effect still occurs in the continuation of the \( B_v \) curve beyond the \( D_1 \) dissociation limit, now due to the mixing between continuum wave functions describing the vibrational motion in the \( 0^+_u (D_1) \) state, with bound vibrational wave functions in

Through use of the mapped FHG method, the eigenvalues of the Hamiltonian 5.1 are calculated up to the dissociation limit \( (5s + 5p^2P_{1/2}) \), hereafter referred to as \( D_1 \) limit (indeed, our choice for an enveloping potential excludes an accurate representation of continuum levels). We have considered a grid extending from 5 to 200\(a_0\), and found convergence for the value \( \beta = 0.5 \) of the mapping parameter. With such values, 525 bound vibrational levels can be found, the upper one having a binding energy \( E_v (v = 524) = -0.015 \text{ cm}^{-1} \).

We present in Fig. 9 the rotational constants \( B_v = 1/(2\mu (R^2)) \) for the vibrational levels (assuming \( J = 0 \)) computed in three different cases: for Hund’s case \( a \) or Hund’s case \( c \) coupling schemes, considering two independent vibrational channels and for the coupled channels. The independent channel calculations yield two curves, rather different in the case of \( A^1\Sigma_u^+ \) and \( b^3\Pi_u \) channels, more similar and even crossing in case of the \( 0^+_u (5s + 5p^2P_{1/2}) \) channels—hereafter referred to as \( 0^+_u (D_1) \) and \( 0^+_u (D_2) \). Coupled-state calculations show that the spin-orbit coupling has a strong effect and introduces important —

FIG. 8. The Rb\(_2\) potential curves without (a) and with (b) spin–orbit coupling. (a) Hund’s case \( a \) \( A^1\Sigma_u^+ (5s + 5p) \) (broken line) and \( b^3\Pi_u (5s + 5p) \) (dash–dotted line) curves from Ref. 40. (b) Hund’s case \( c \) \( 0^+_u (D_1) \) and \( 0^+_u (D_2) \) potential curves correlated, respectively, to the dissociation limits \( (5s + 5p^2P_{1/2}) \) and \( (5s + 5p^2P_{3/2}) \). A vibrational level close to the \( D_1 \) limit, and its turning point in the \( 0^+_u (D_2) \) potential, are displayed for illustration.

FIG. 9. Rotational constants \( B_v \) (in \text{cm}^{-1}) for vibrational levels in the Rb\(_2\) \( A^1\Sigma_u^+ \) and \( b^3\Pi_u \) [or, equivalently, \( 0^+_u (D_1) \) and \( 0^+_u (D_2) \)] potential curves of Fig. 8 computed: neglecting fine structure coupling (Hund’s case \( a \) : full lines); neglecting radial coupling (Hund’s case \( c \) : dashed lines); and considering two coupled channels (circles). The energy of the levels is referred to the \( (5s + 5p) \) dissociation limit.

FIG. 10. The same as Fig. 9, close to the \( (5s + 5p^2P_{1/2}) \) dissociation limit (labeled \( D_1 \) and located at energy \( E = -158.4 \text{ cm}^{-1} \)).
the $0^+_v (D_2)$ state. The present time-independent formalism is not providing information on the predissociation lifetime of such levels. But we can solve the time-dependent Schrödinger equation defined from the Hamiltonian in Eq. (5.1) and from a given eigenfunction taken as an initial state compute the autocorrelation function, as already performed in our previous work.\textsuperscript{22} The limited energy range of the representation then appears as an advantage for such calculations. The lifetime is most easily extracted from the exponential behavior of the autocorrelation function, and this example shows clearly the advantage of the technique. Detailed calculations of the lifetimes and analysis of the predissociation process will be published in a forthcoming paper.

VI. CONCLUSION

(i) The theoretical treatment of cold atom collisions and photoassociation processes leads us to treat the relative motion of two nuclei in regions of space where the kinetic energies differ by several orders of magnitude. Grid methods have to be modified by compressing the number of points in order to reduce the computational effort. In the present paper we describe a mapping procedure in which the change of variable closely follows the variation of the local de Broglie wavelength as a function of the internuclear distance. We have discussed the implementation of this procedure within a Fourier Grid Hamiltonian method for determination of energies and wave functions of loosely bound vibrational states in alkali dimer molecules. Reducing by $n$ the number of points in a numerical method relying upon diagonalization procedure results into reducing by $n^3$ the computational effort.

(ii) In case of single channel calculations, we have discussed two possible choices for the definition of a new grid and transformation of the Hamiltonian: one is using a numerical change of variable considering the real potential of the problem; the other one is analytical and based upon the asymptotic $R^{-n}$ behavior of the potential. The latter procedure was recently used by Tiesinga \textit{et al.}\textsuperscript{18} Due to the divergence of $R^{-n}$ at short distances, the numerical mapping procedure has been demonstrated to be more efficient. It yields better optimization of the phase space, and avoids an unnecessary increase of the spectral range of the Hamiltonian.

(iii) We have discussed the convergence tests and accuracy of the method, showing that very accurate results can then be obtained for binding energies and wave functions of vibrational levels, where the classical motion extends as far as $500a_0$, with a minimal number of points, typically less than twice the number of nodes of the wave function.

(iv) The numerical mapping procedure has next been generalized to problems involving several channels, through the use of an enveloping potential. An example of an application to the perturbations in the Rb$_2$ spectrum has been given. We have shown that the method can easily be extended to the computation of predissociation lifetimes.

(v) In contrast with recent work by Tiesinga \textit{et al.}\textsuperscript{18} the accent in the present paper was put on the mapping procedure rather than the method to extract eigenvalues. We have shown the advantage of maintaining a Hermitian Hamiltonian operator, and discussed the efficiency of a numerical mapping procedure in view of optimizing the representation. The diagonalization procedure, having uniform convergence with respect to eigenvalue extraction, could be used to check the global performance of the mapping. The quality of the wave functions obtained by interpolation using Fourier transformation is also an original aspect of this work.

(vi) In the case of two coupled channels, the method is presently formulated for diabatic calculations. Further development should consider a formulation using the $d/dR$ coupling, where the advantage of the present mapping procedure maintaining a symmetric Hamiltonian operator will clearly be manifested.

(vii) In future work we will address the problem of propagation either for filtering the eigenvalues in a given energy range, in the spirit of Ref. 44, or for the treatment of time-dependent problems related to cold collisions and predissociation. The numerical mapping procedure developed here will help to maintain a small as possible the spectral range of the Hamiltonian.

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APPENDIX: THE KINETIC OPERATOR IN THE FGH REPRESENTATION

The Hamiltonian of Eq. (2.17), written in Fourier grid representation, is real but nonsymmetric. In order to show it, we write each term of the Hamiltonian this representation:
Here elements \( T_{i,j} \) are same as in Eqs. (2.3) and (2.4). Indexes \( i \) and \( j \) are introduced nonsymmetrically because of \( 1/J^2(x_i) \). The term

\[
\langle \varphi_i | \frac{1}{2 \mu J^2} \frac{d^2}{dx^2} | \varphi_j \rangle = \frac{1}{J^2(x_i)} T_{i,j}.
\]  

(A1)

is also nonsymmetric. (Note that the first derivative in FGH is antisymmetric\(^\text{19}\)). Being diagonal, the operator \( V(x) \) is symmetric.

Consider now the Hamiltonian of Eq. (2.20). The new potential \( \tilde{V} \) is diagonal. To evaluate the new kinetic operator, note that for any function \( F(x) \) the second derivative in FGH will be

\[
F''(x_n) = \left( \frac{d^2}{dx^2} F(x) \right)_n = -\frac{4\pi^2}{NL^2} \sum_{k=-N/2+1}^N \sum_{s=1}^N F(x_s) k^2 \exp \left( \frac{2\pi(n-s)k}{N} \right). 
\]  

(A3)

and for \( F(x) \varphi(x) \) function,

\[
\left( \frac{d^2}{dx^2} F(x) | \varphi(x) \rangle \right)_n = \left( \frac{d^2}{dx^2} \langle F(x) \varphi(x) \rangle \right)_n = -\frac{4\pi^2}{NL^2} \sum_{k=-N/2+1}^N \sum_{s=1}^N F(x_s) k^2 \times \exp \left( \frac{2\pi(n-s)k}{N} \right) \varphi_i(x_s). 
\]  

(A4)

For the scalar product \( \langle | \rangle \):

\[
\langle \varphi_m | \frac{d^2}{dx^2} F(x) | \varphi_i \rangle = -\frac{4\pi^2}{NL^2} \sum_{k=-N/2+1}^N \sum_{s=1}^N F(x_s) k^2 \times \exp \left( \frac{2\pi(n-s)k}{N} \right) \varphi_i(x_s).
\]  

(A5)

The kinetic operator in the equation is

\[
\langle \varphi_m | -\frac{1}{2\mu} \frac{1}{J^2} \frac{d^2}{dx^2} + \frac{1}{2\mu J^2} | \varphi_i \rangle = \frac{\pi^2}{\mu NL^2} \left( \frac{1}{J^2(x_m)} + \frac{1}{J^2(x_i)} \right) \sum_{k=-N/2+1}^N k^2 \times \exp \left( \frac{2\pi(m-l)k}{N} \right). 
\]  

(A6)

The sum here is\(^\text{19}\)}

\[
\sum_{k=-N/2+1}^N k^2 \exp \left( \frac{2\pi(m-l)k}{N} \right) = \frac{N(N+1)(N+2)l^2}{2l}\quad m\neq l;
\]  

(A7)

\[
\sum_{k=-N/2+1}^N k^2 \exp \left( \frac{2\pi(m-l)k}{N} \right) = \frac{N^2+2}{12}, \quad m=l.
\]  

(A8)

From Eqs. (A6)–(A8), we obtain the expressions (2.22) and (2.23) for the kinetic energy operator (2.20). Expressions (2.22) and (2.23) are symmetrical over \( i \) and \( j \).
41 C. Amiot (private communication).