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Time-dependent variational principles and conservation laws in wavepacket dynamics

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Abstract. A criterion for the equivalence of time-dependent variational principles in current use in chemistry and physics is demonstrated. Conservation laws are considered and it is shown that under certain conditions quantal conservation laws also hold for the time evolution derived from the variational principle. The formalism is applied to an N-dimensional spherical Gaussian wavepacket. A numerical example for the three-dimensional spherical Gaussian potential well is worked out to illustrate the dynamics and the role of conservation laws.

1. Introduction

Time-dependent variational principles generate approximate solutions to the time-dependent Schrödinger equation. Provided they lead to practical and accurate time propagation schemes they can be very useful in a variety of problems [1]. Indeed, by Fourier transforming various types of time correlation functions one obtains the corresponding time-independent physical properties (energy spectrum, cross sections, etc). In the molecular physics literature, especially in recent applications of wavepacket techniques, the time-dependent variational principle attributed to McLachlan has been implemented [2-4]. In nuclear physics a different development took place based on the principle of stationary action or Hamilton principle using a quantum mechanical Lagrangian. It has been applied to time-dependent Hartree-Fock and other group theoretical nuclear structure models [5, 6].

Our objective here is twofold. First we will show that when the time evolution of a parametrised wavefunction is restricted to the time dependence of a set of real 'complementary parameters' the above-mentioned principles generate the same evolution equations. This is intended to show that the discussion of conservation laws that is to follow is valid in either approach. Secondly we will argue that the stationary action formulation has significant formal advantages because of its resemblance to the classical Hamilton formalism. One of those advantages is to provide a framework for the study of the conservation laws in the classical formalism and their relation to quantum conservation laws. We work out a numerical illustration for a three-dimensional Gaussian wavepacket moving in a potential well and focus our attention on the angular momentum conservation laws.

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2. The equivalence of the time-dependent variational principles

It has been pointed out [7] that the equivalence of the aforementioned time-dependent principles is non-trivial, i.e. it is conditional upon the manifold of wavefunctions to which one applies the variational principle. In [7] the authors show that the equivalence holds in the case of a complex, analytic parametrisation of the wavefunction. We consider the case of real parameters and show that there is equivalence provided the parameters satisfy a condition that we refer to as the 'complementarity' of the parameters.

In order not to complicate the variational equations we will assume in the following that all wavefunctions $\phi(x, t)$, where x stands for all the system's degrees of freedom, are normalised at all times. With this convention the principle of stationary action, or Hamilton's principle, requires the variation of the action, i.e. the integral of the quantum Lagrangian, to be zero [2]

$$\delta_\phi \left(\oint_{t_1}^{t_2} \mathrm{d}t \, \langle \phi(t) | \mathrm{i}h \, \partial/\partial t - \mathbf{H} | \phi(t) \rangle \right) = 0 \tag{1}$$

where the Dirac bracket implies integration over x. In the literature one usually refers to (1) as the TDVP principle. Carrying out the variation leads to

$$\mathrm{Re} \langle \delta\phi | \mathrm{i}\hbar \, \partial/\partial t - \mathbf{H} | \phi \rangle = 0. \tag{2}$$

It is easy to show that arbitrary variations $\delta\phi$ of the normalised states $\phi(x, t)$ yield the time-dependent Schrödinger equation provided the correct time dependence of the phase is taken into account by the formula

$$\psi = \phi \exp \left[\frac{\mathrm{i}}{\hbar} \left(\int^{t} \langle \phi | \mathrm{i}\hbar \, \partial/\partial t' - \mathbf{H} | \phi \rangle \, \mathrm{d}t' \right) \right]. \tag{3}$$

If $\phi(x, t)$ is restricted to a predetermined region of the Hilbert space, the variational principle will generate an approximate but variationally optimal time evolution of a given state. Here we will consider wavefunctions that depend on time via a set of N real parameters only, i.e.

$$\phi(x, t) = \phi(x | \alpha_1(t), \alpha_2(t), \ldots, \alpha_N(t)) = \phi(x | \alpha(t)). \tag{4}$$

The nature and the physical significance of the parameters $\alpha(t) = \{\alpha_1(t), \ldots, \alpha_N(t)\}$ will depend upon the problem at hand. A phase parameter is excluded here because the time-dependent phase can be taken into account separately by (3). The action integral in (1) now becomes a functional of the path $\alpha(t)$ in the parameter manifold. The variational principle requires the action path to be stationary, much like the trajectory of a system in classical mechanics. In setting up the equations of motion for $\alpha(t)$, two quantities enter the theory [5]. The first one is the function

$$H(\alpha) = \langle \phi(\alpha) | \mathbf{H} | \phi(\alpha) \rangle \tag{5}$$

while the second one is the tensor (with $\hbar$ set equal to unity)

$$\eta_{mn}(\alpha) = \mathrm{i} \left(\left\langle \frac{\partial \phi}{\partial \alpha_m}(\alpha) \middle| \frac{\partial \phi}{\partial \alpha_n}(\alpha) \right\rangle - \left\langle \frac{\partial \phi}{\partial \alpha_n}(\alpha) \middle| \frac{\partial \phi}{\partial \alpha_m}(\alpha) \right\rangle \right). \tag{6}$$

In these definitions, as in the following, we suppress the time dependence of the parameters. Since $\eta_{mn}(\alpha)$ depends solely on $\phi(\alpha)$, while $H(\alpha)$ involves the Hamiltonian, one can say that (6) represents the kinematical and (5) the dynamical aspects

of the time evolution of the parameters. In terms of the above concepts the equations of motion in the parameter space can be written as

$$\sum_{n=1}^{N} \eta_{mn}(\alpha)\frac{\mathrm{d}\alpha_n}{\mathrm{d}t} = \left\langle \frac{\partial\phi}{\partial\alpha_m}(\alpha)\middle|\mathbf{H}\middle|\phi(\alpha)\right\rangle + \left\langle \phi(\alpha)\middle|\mathbf{H}\middle|\frac{\partial\phi}{\partial\alpha}(\alpha)\right\rangle = \frac{\partial H}{\partial\alpha_m}(\alpha). \tag{7}$$

Provided $\eta_{mn}(\alpha)$ is invertible for all α, these can be re-written as a set of coupled first-order ordinary differential equations of the form

$$\frac{\mathrm{d}\alpha_m}{\mathrm{d}t} = \sum_{n=1}^{N} \xi_{mn}(\alpha)\frac{\partial H}{\partial\alpha_n}(\alpha) \tag{8}$$

where ξ is the inverse tensor to η†. Observe that since η is antisymmetric, so is ξ. The latter tensor now allows for the definition of a generalised Poisson bracket

$$\{f, g\} = \sum_{m,n=1}^{N} \frac{\partial f}{\partial\alpha_m}\xi_{mn}(\alpha)\frac{\partial g}{\partial\alpha_n} \tag{9}$$

of any two functions f and g of α. In terms of this Poisson bracket the equations of motion take the form

$$\frac{\mathrm{d}\alpha_n}{\mathrm{d}t} = \{\alpha, H\}. \tag{10}$$

Thus the variational principle has led us from a manifold in Hilbert space to a parameter phase space in which time evolution is described classically by a generalised Poisson bracket. The strong parallelism between the TDVP (10) and classical Hamiltonian dynamics allows for the study of a quantum system as if it were a classical problem. We will return to this aspect later.

The variational principle formulated by McLachlan, reconsidered by Heller [3, 4] for the propagation of Gaussian wave packets, and also by Sawada *et al* [8], who refer to it as the minimum error method, states that

$$\delta_\theta[\|(\mathrm{i}\,\partial/\partial t - \mathbf{H})\phi\|^2] = 0 \tag{11}$$

where $\theta = \partial\phi/\partial t$ is the only quantity to be varied. Clearly (11) is satisfied if $\phi(t)$ is a solution to Schrödinger's equation. Carrying out the variation with respect to θ yields

$$\mathrm{Im}[\langle\delta\theta|\mathrm{i}\theta - \mathbf{H}\phi\rangle] = 0 \tag{12}$$

from which one also recovers Schrödinger's equation if one considers arbitrary variations of θ. As before, the correct phase is given by (3). For parametrised states (4) it is clear that θ is a function of both the α_m and the $\mathrm{d}\alpha_m/\mathrm{d}t$. Therefore the variation of θ is

$$\delta\theta\left(\alpha, \frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = \sum_{n=1}^{N} \frac{\partial\theta}{\partial\alpha_n}\left(\alpha, \frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)\delta\alpha_n + \frac{\partial\theta}{\partial(\mathrm{d}\alpha_n/\mathrm{d}t)}\left(\alpha, \frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)\delta\left(\frac{\mathrm{d}\alpha_n}{\mathrm{d}t}\right). \tag{13}$$

However, the first term can be deleted here. Indeed since $\phi(t)$ is required to be fixed in the variation with respect to θ, one has $\delta\alpha_m = 0$ for all m. Therefore by deleting the first term and since $\theta = (\partial\phi/\partial\alpha_n)(\mathrm{d}\alpha_n/\mathrm{d}t)$, the $\delta\theta$ reduces to

$$\delta\theta\left(\alpha, \frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = \sum_{n=1}^{N} \frac{\partial\phi}{\partial\alpha_n}\delta\left(\frac{\mathrm{d}\alpha_n}{\mathrm{d}t}\right). \tag{14}$$

† In order for η to be invertible the number of parameters must be even.

For arbitrary variations $\delta(\mathrm{d}\alpha_n/\mathrm{d}t)$ one obtains the evolution equations:

$$\sum_{n=1}^{N} \tau_{mn}(\alpha)\frac{\mathrm{d}\alpha_n}{\mathrm{d}t} = \left\langle \frac{\partial\phi}{\partial\alpha_m}(\alpha)|\mathbf{H}|\phi(\alpha)\right\rangle - \left\langle \phi(\alpha)|\mathbf{H}|\frac{\partial\phi}{\partial\alpha_m}(\alpha)\right\rangle \tag{15}$$

where τ is the counterpart of η, defined by

$$\tau_{mn}(\alpha) = \mathrm{i}\left(\left\langle \frac{\partial\phi}{\partial\alpha_m}(\alpha)\middle|\frac{\partial\phi}{\partial\alpha_n}(\alpha)\right\rangle + \left\langle \frac{\partial\phi}{\partial\alpha_n}(\alpha)\middle|\frac{\partial\phi}{\partial\alpha_m}(\alpha)\right\rangle\right). \tag{16}$$

A priori the TDVP (7) and McLachlan (15) equations of motion are totally different and in general they lead to a different time evolution of the parameters α. However, in the literature [8, 9] both variational principles have been applied to identical model systems, e.g. Gaussian wavepackets moving in a Morse potential, and have yielded the same qualitative results (i.e. similar trajectories, energy conservation etc). This seems to imply that under certain conditions the two principles are equivalent. Detailed investigation in the case of the simplest Gaussian wavepacket, which we can write as

$$\phi(\alpha_1 = q, \alpha_2 = p) = \exp(-x^2/2 + qx + \mathrm{i}px) \tag{17}$$

omitting phase and normalisation factors, has shown that the equivalence is due to the existence of a 'complementarity' between the parameters in the sense that

$$\mathrm{i}\frac{\partial\phi}{\partial q} = \frac{\partial\phi}{\partial p}. \tag{18}$$

We can now generalise this result as follows. McLachlan's principle (11) and the principle of stationary action (1) are equivalent if the manifold of wavefunctions ϕ (save for normalisation and phase factors) can be parametrised by pairs of complementary parameters. This means that a transformation exists from (α_j) $j = 1, \ldots, N$ to a set (x_k, y_k) with $k = 1, \ldots, N/2$ such that

$$\mathrm{i}\frac{\partial\phi}{\partial x_k} = \frac{\partial\phi}{\partial y_k}. \tag{19}$$

It is clear that in order for complementarity to be possible, the number of parameters N must be even. Given a parametrisation $\phi = \phi(\alpha_1, \ldots, \alpha_N)$, it is not always trivial to find a transformation to an (x_k, y_k) set or even to prove its existence (cf, e.g. the Gaussian wavepacket (31)).

With condition (19) it is straightforward to prove that McLachlan's and the stationary action principles are equivalent, i.e. yield identical equations of motion. Assume (6), (7) and (15), (16) have been derived in a parameter set with complementarity, i.e. $\alpha_j = x_j$ for $j = 1, \ldots, N/2$ and $\alpha_j = y_j$ for $j = (N/2)+1, \ldots, N$. Let α_m and α_n be complementary coordinates and substitute in the McLachlan's equations (15) and (16)

$$\frac{\partial\phi}{\partial\alpha_m} = \begin{cases} -\mathrm{i}\dfrac{\partial\phi}{\partial\alpha_n} & m = 1, \ldots, \dfrac{N}{2} \qquad (20) \\ \mathrm{i}\dfrac{\partial\phi}{\partial\alpha_n} & m = \dfrac{N}{2}+1, \ldots, N. \qquad (21) \end{cases}$$

After redefining indices, one arrives at

$$\mathrm{i}\sum_{n=1}^{N}\left(\left\langle\frac{\partial\phi}{\partial\alpha_m}\middle|\frac{\partial\phi}{\partial\alpha_n}\right\rangle - \left\langle\frac{\partial\phi}{\partial\alpha_n}\middle|\frac{\partial\phi}{\partial\alpha_m}\right\rangle\right)\frac{\mathrm{d}\alpha_n}{\mathrm{d}t} = \left\langle\frac{\partial\phi}{\partial\alpha}|\mathbf{H}|\phi\right\rangle + \left\langle\phi|\mathbf{H}|\frac{\partial\phi}{\partial\alpha_m}\right\rangle \tag{22}$$

which are precisely the TDVP equations (6), (7). Evidently, the same substitution takes one back from the TDVP to McLachlan's equations (15), (16), thus establishing their equivalence.

Many applications in molecular physics deal with Gaussian wavepackets in various dimensions. The wavepackets may have position and linear momentum as parameters, or additionally the width and an associated momentum, as in (31) below. The condition of complementarity is fulfilled for such packets. This can be verified explicitly on (31) by removing norm and phase factors and taking $\{x_k\}=\{(N/2w^2)\boldsymbol{q},\ (N/4w^2)\}$ and $\{y_k\}=\{(\boldsymbol{p}-(4/w)\boldsymbol{q}), (-Nu/2w)\}$. Thus we can choose either the 'stationary action' or McLachlan's formulation to obtain equations of motion for the wavepacket parameters. In the case of Gaussian wavepackets yet another method exists for deriving the equations of motion, namely the 'method of moments' [10]. Again this method can be shown to be equivalent to the other two [11].

A formal advantage of the 'stationary action' formulation is the Hamilton-like form (10) of the equations. We will use this fact in the next section to give a general discussion of conservation laws associated with the TDVP dynamics on a manifold M of states $\phi(\alpha)$. The results obtained also apply of course to McLachlan dynamics in case of equivalence as, for example, for Gaussian wavepackets.

3. Conservation laws

In analogy with the definition of the TDVP Hamiltonian, one can associate with any quantum observable a function $A(\alpha)$ on the parameter phase space

$$A(\alpha)=\langle\phi(\alpha)|\mathbf{A}|\phi(\alpha)\rangle. \tag{23}$$

The variation in time of such a function along the trajectory $\alpha(t)$ is easily computed using the equations of motion (8)

$$\frac{\mathrm{d}}{\mathrm{d}t}A(\alpha(t))=\sum_{m=1}^{N}\frac{\partial A}{\partial\alpha_m}(\alpha(t))\frac{\mathrm{d}\alpha_m}{\mathrm{d}t}=\sum_{m,n=1}^{N}\frac{\partial A}{\partial\alpha_m}(\alpha(t))\xi_{mn}(\alpha(t))\frac{\partial H}{\partial\alpha_n}(\alpha(t)). \tag{24}$$

The TDVP time evolution of $A(\alpha)$ is therefore generated by the differential equation

$$\frac{\mathrm{d}}{\mathrm{d}t}[A_{\mathrm{TDVP}}(\alpha(t))]=\{A_{\mathrm{TDVP}}(\alpha(t)), H(\alpha(t))\}. \tag{25}$$

Thus $H(\alpha)$ can be interpreted as the generator of time translations and the structure of (25) is exactly as in classical mechanics. From a quantal point of view (25) should be considered as an approximation to the generalised Ehrenfest equation

$$\frac{\mathrm{d}}{\mathrm{d}t}A_{\mathrm{Quantum}}(t)=\langle\phi(t)|-\mathrm{i}[\mathbf{A},\mathbf{H}]|\phi(t)\rangle \tag{26}$$

for the time evolution of the expectation value $A_{\mathrm{Quantum}}(t)=\langle\phi(t)|\mathbf{A}|\phi(t)\rangle$ of the operator $\mathbf{A}$ with respect to the exact time evolved state $\phi(t)=\exp(-\mathrm{i}\mathbf{H}t)\phi(\alpha)$. If the manifold of the $\phi(\alpha)$ is not the entire Hilbert space the TDVP and quantal time evolution differ, resulting in non-zero deviations between the TDVP and quantal expectation values. The magnitude of these deviations can be considered as a measure of the quality of the TDVP time evolution.

Of special interest in any dynamical theory are conserved quantities or so-called constants of the motion. In the TDVP formalism it follows from (26) that conserved quantities are characterised by vanishing brackets with $H(\alpha)$. One can use the constants of the motion to simplify the interpretation of the TDVP trajectories. Indeed, as in classical mechanics, a trajectory $\alpha(t)$ must lie in the submanifold of phase space described by the intersection of hypersurfaces corresponding to constant values of the conserved quantities. However, when considering TDVP dynamics as approximate quantum dynamics, one should pay attention to those TDVP quantities that correspond to quantal constants of motion, i.e. to functions $A(\alpha)$ associated with operators $\mathbf{A}$ that commute with the Hamiltonian $\mathbf{H}$. It may happen that a quantity is both TDVP and quantum conserved. A trivial example is the energy since $H(\alpha)$ has vanishing bracket with itself and $\mathbf{H}$ has vanishing commutator with itself. In general, however, one can not guarantee that A_{TDVP} is a TDVP constant of the motion if the corresponding $\mathbf{A}$ commutes with $\mathbf{H}$. It follows from (25) and (26) that at least a sufficient condition of simultaneous conservation of A_{TDVP} and A_{Quantum} can be given. Indeed if

$$\{A(\alpha), H(\alpha)\} = \langle \phi(\alpha)| -\mathrm{i}[\mathbf{A}, \mathbf{H}]|\phi(\alpha)\rangle \tag{27}$$

$$[\mathbf{A}, \mathbf{H}] = 0 \tag{28}$$

the right-hand side of (25) vanishes along any trajectory. Clearly for (27) to hold there must exist a compatibility between the choice of $\mathbf{A}$ and the structure of the manifold of states $\phi(\alpha)$. Kramer and Saraceno [5] have studied the case in which $\phi(\alpha)$ is constructed out of a reference state $\phi(x|0)$ through the action of Lie group operators as follows:

$$\phi(x|\alpha) = \exp\left(\mathrm{i}\sum_{m=1}^{N} \alpha_m \mathbf{A}_m\right)\phi(x|0) \tag{29}$$

where the $\mathbf{A}_m$ are the generators of the Lie group (cf also the appendix). One can then prove (under conditions specified in [5]) that for the phase space functions $A_m(\alpha)$ corresponding to the generators $\mathbf{A}_m$, (27) is satisfied. Hence one can conclude that if $\mathbf{H}$ commutes with a generator of the Lie group in (29), that operator defines a conservation law for both the TDVP and the exact quantal motion.

4. An illustration

We develop the formalism of the previous sections for the Hamiltonian

$$\mathbf{H} = -\frac{1}{2m}\Delta_r + V(\boldsymbol{r}) \tag{30}$$

and the Gaussian wavepacket (GWP)

$$\phi(\boldsymbol{r}|\boldsymbol{p}, \boldsymbol{q}, u, w) = \left(\frac{N}{2\pi w^2}\right)^{N/4} \exp\left(-\frac{(N - 2\mathrm{i}uw)}{4w^2}\right)(\boldsymbol{r}-\boldsymbol{q})^2 + (\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{r}). \tag{31}$$

Here $\boldsymbol{r}$ is an N-dimensional vector, m a mass parameter and $V(\boldsymbol{r})$ an arbitrary local potential. Observe that the form for $\mathbf{H}$ includes the case of a many-body system provided the components of $\boldsymbol{r}$ are mass scaled particle coordinates. The GWP wavefunction contains $2N+2$ parameters (in the previous section this number was denoted by N) and it is the spherical extension of the most general GWP in one dimension, which

we introduced in [9]†. For the one-dimensional case it was shown that the TDVP time evolution of (31) was formally equivalent to the classical mechanics of a particle of mass m in a two-dimensional potential. The TDVP equations then reduced to classical Hamiltonian equations in which the position and momentum (q and p) and the width and dilational momentum (w and u) acted as conjugate pairs of variables. To a great extent these conclusions carry over to the case of the N-dimensional GWP (31). Indeed the Hamilton function is given by

$$H(\boldsymbol{p}, \boldsymbol{q}, u, w) = \frac{p^2}{2m} + \frac{u^2}{2m} + U(\boldsymbol{q}, w) \tag{32}$$

$$U(\boldsymbol{q}, w) = \frac{N^2}{8mw^2} + (2\pi)^{-N/2} \int \mathrm{d}\boldsymbol{r} \exp(-\tfrac{1}{2}r^2)\, V(w\boldsymbol{r} + \boldsymbol{q}) \tag{33}$$

which is the Hamiltonian of a particle of mass m moving in an $(N+1)$-dimensional potential $U(\boldsymbol{q}, w)$ that contains the Gauss transform of the original potential $V(\boldsymbol{r})$ and a localisation term inversely proportional to the square of the GWP width w. The spatial parameters of the GWP, the position vector $\boldsymbol{q}$ and the width w, have conjugate momenta $\boldsymbol{p}$ and u, the square of which determine the kinetic energy part of H. Because of the judicious choice of parametrisation, the TDVP bracket reduces to the Poisson form

$$\{A, B\} = \sum_{j=1}^{N} \left(\frac{\partial A}{\partial q_j} \frac{\partial B}{\partial p_j} - \frac{\partial A}{\partial p_j} \frac{\partial B}{\partial q_j} \right) + \left(\frac{\partial A}{\partial w} \frac{\partial B}{\partial u} - \frac{\partial A}{\partial u} \frac{\partial B}{\partial w} \right). \tag{34}$$

Combining this result with the expression (32) for the Hamiltonian function yields the TDVP equations of motion for the GWP parameters

$$\begin{aligned} \frac{\mathrm{d}q_j}{\mathrm{d}t} &= \frac{1}{m} p_j & \frac{\mathrm{d}p_j}{\mathrm{d}t} &= -\frac{\partial U}{\partial q_j}(\boldsymbol{q}, w) \\ \frac{\mathrm{d}w}{\mathrm{d}t} &= \frac{1}{m} u & \frac{\mathrm{d}u}{\mathrm{d}t} &= -\frac{\partial U}{\partial w}(\boldsymbol{q}, w). \end{aligned} \tag{35}$$

These are classical Hamiltonian equations containing the TDVP forces, i.e. the gradients of the potential U with respect to q_i and w, giving the rate of change of the momenta p_i and u.

Along a trajectory $\boldsymbol{q}(t)$, $\boldsymbol{p}(t)$, $w(t)$, $u(t)$ one can check whether a TDVP function (23) is conserved or not. Of particular interest are those quantities which are quantum mechanically conserved but for which (27) does not hold such that non-zero deviations between TDVP and quantum expectation values may arise. We first consider the angular momentum operator $\mathbf{L} = \boldsymbol{r} \times (1/\mathrm{i})\boldsymbol{\nabla}$. The phase space angular momentum $\boldsymbol{L}(\alpha) = \langle \phi(\alpha) | \mathbf{L} | \phi(\alpha) \rangle$ of the wavepacket (31) is equal to the classical angular momentum of the centre of the wavepacket $\boldsymbol{L}(\boldsymbol{q}, \boldsymbol{p}) = \boldsymbol{q} \times \boldsymbol{p}$. If $\mathbf{H}$ is rotationally invariant, i.e. if $V(\boldsymbol{r}) = V(r)$, it commutes with the components $\mathbf{L}_k$ and the square $\mathbf{L}^2$ of the angular momentum operator. It can be shown, by referring to the group theoretic construction of the previous section (cf the appendix) or by explicit calculation, that whereas for $\mathbf{L}_k$ we have

$$\{H, L_k\} = \langle \phi(\alpha) | [\mathbf{H}, \mathbf{L}_k] | \phi(\alpha) \rangle = 0 \tag{36}$$

† During the refereeing process of the present paper we published the TDVP formalism for the most general GWP [12].

this is not necessarily so for $\mathbf{L}^2$:

$$\{H, L^2\} \neq \langle \phi(\alpha) | [\mathbf{H}, \mathbf{L}^2] | \phi(\alpha) \rangle = 0 \tag{37}$$

due to the fact that $\langle \phi(\alpha) | \mathbf{L}_k | \phi(\alpha) \rangle^2 \neq \langle \phi(\alpha) \mathbf{L}_k^2 | \phi(\alpha) \rangle$.

In view of the properties mentioned above, the angular momentum operators will allow us to illustrate all features of conservation laws in the TDVP framework.

5. Numerical results

Explicit calculations were performed for a three-dimensional Gaussian well. For a rotationally invariant potential $V(r)$, the TDVP potential U depends on q instead of $\boldsymbol{q}$, and w only. In our case this gives

$$V(r) = V_0 \exp[-r^2/(2a^2)] \tag{38}$$

$$U(q, w) = \frac{9\hbar^2}{8mw^2} + V_0 \left(\frac{a^2}{w^2 + a^2} \right)^{3/2} \exp\left[-\frac{3}{2} \left(\frac{q^2}{w^2 + 3a^2} \right) \right]. \tag{39}$$

From now on we use SI units, hence the explicit occurrence of $\hbar$, which was taken to be unity in all previous formulae. The depth and width of the well are fixed at an order of magnitude appropriate for the vibrations of a light diatomic molecule, i.e. $V_0 = -1 \times 10^{-18}$ J, $a = 0.7 \times 10^{-10}$ m, similarly the mass parameter corresponds to the reduced mass for such a molecule, $m = 1 \times 10^{-27}$ kg. With these values the GWP parameters evolve on a time scale of 1×10^{-15} s.

The propagation of the GWP according to the equations of motion (35) is described by the functions $\boldsymbol{q}(t)$, $\boldsymbol{p}(t)$, $w(t)$ and $u(t)$. As the angular momentum vector $\boldsymbol{L}$ is conserved, the position vector $\boldsymbol{q}(t)$ moves in a plane perpendicular to $\boldsymbol{L}$ with constant sectorial velocity, just as in the case of a classical particle in a central potential. We shall take the q_3 axis along $\boldsymbol{L}$ and use polar coordinates $q_1 = q \cos\theta$, $q_2 = q \sin\theta$. The Hamiltonian (32) can then be written with radial momentum $p_{\text{rad}} = m\dot{q}$, as

$$H(\boldsymbol{p}, \boldsymbol{q}, u, w) = \frac{p_{\text{rad}}^2}{2m} + \frac{u^2}{2m} + \frac{L^2}{2mq^2} + U(q, w) \tag{40}$$

and hence the motion of the GWP can be reduced to a problem of two degrees of freedom q and w, formally equivalent to the motion of a classical particle with mass m in a two-dimensional effective potential $U_{\text{eff}}(q, w) = L^2/2mq^2 + U(q, w)$.

For the case of the Gaussian well (38) we have considered the WP propagation in three different energy regions. A low-energy regime ($E \cong V_0$), an intermediate region close to the point of inflection of V ($E \cong \frac{1}{2}V_0$) and a high-energy region ($E \cong 0$). For energies near the bottom of the well a near harmonic behaviour is found. This regime has been studied in detail both numerically and analytically and needs no further comment. The most typical behaviour of the time evolution of the various quantities is found in the intermediate range. For higher energies these features remain but become less conspicious. We will therefore concentrate our investigations on the intermediate-energy range, which is also interesting because of the onset of the breakdown of the harmonic approximation.

In figure 1 we show a typical orbit in the (q_1, q_2) plane of intermediate energy $E = 0.63\ V_0$ and initial conditions $q_1 = 0.5 \times 10^{-10}$, $q_2 = 0$, $w = 1.2 \times 10^{-11}$, $p_1 = p_2 = 0.7 \times 10^{-23}$, $u = 0$. Three types of motion are clearly visible in the form of a pulsating

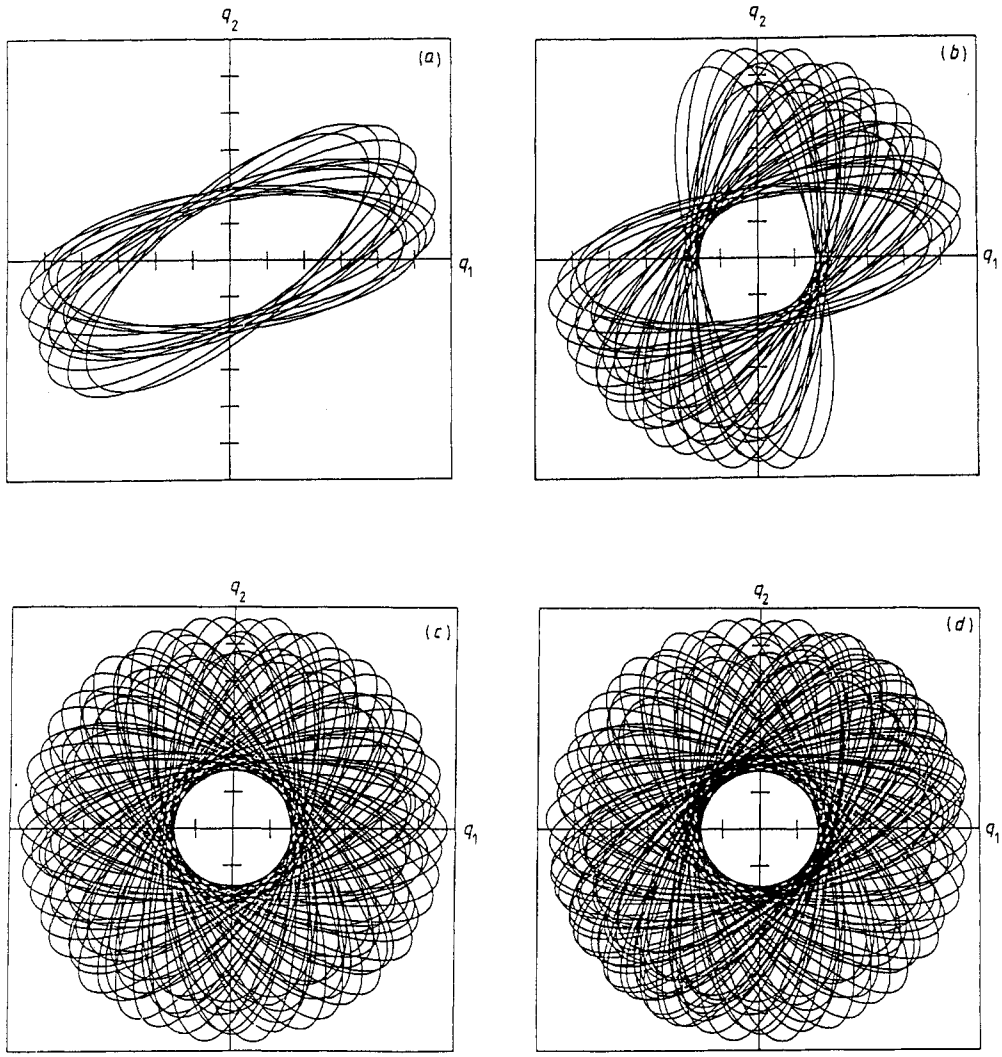

Figure 1. TDVP trajectory (initial conditions given in text) in the (q_1, q_2) plane with units of 10^{-11} m at successive times, 0.2 ps, 0.7 ps, 1.2 ps and 1.6 ps.

rosette: the trajectory is composed of quasi-ellipses of which the perihelion rotates and oscillates between two extreme radial distances.

If the WP were frozen, i.e. w remains constant and $u = 0$, then, as in the case of a classical particle, $q(t)$ would vary between two fixed values $q_{\min}$ and $q_{\max}$. The perihelion of the orbit would precess uniformly at a fixed distance from the origin. There would thus be two timescales involved: the radial period τ_R and the precession period τ_P. Here however, as a consequence of the typically quantal phenomenon of the spreading of the WP, which is one of the topics under investigation here, the value of w changes in time. In fact, the equations of motion (35) establish a coupling between the q and w degrees of freedom. This coupling results in a modulation of the radial amplitude. The beat frequency associated with the latter aspect of the GWP evolution introduces a third scale τ_B in the TDVP dynamics. Also, the precession is not uniform.

In figure 2(*a*) the function $q_1(t)$ displays the three different timescales: the short radial period $\tau_R(\sim 0.1)$, the long period $\tau_P(\sim 10)$ and the intermediate period $\tau_B(\sim 1)$. From figures 2(*b*) and 2(*c*) we can see the beats superimposed on the rapid oscillation of the radial position q and the width w of the WP. This correlation between q and w is brought out in another way by looking at the q-w section of the phase space (figure 3): the WP trajectory fills an area of which the shape reflects the shrinking of the WP at large radial distance and vice versa. It is noteworthy that w remains finite at all times, so the Gaussian WP remains localised although we are near the inflection point of the potential V, where the harmonic approximation breaks down and the associated WP would spread uncontrollably.

We now focus on the conserved quantities. The conservation of energy is satisfied numerically to a high degree of accuracy (see figure 4). The total energy is composed of three parts: the kinetic energy of translation, the kinetic energy of dilation and the potential energy. Each part is a rapidly fluctuating quantity, as can be seen from figure 4. The constancy of the total energy therefore is a good test for the accuracy of the numerical calculations. It should be remarked that kinetic energy is being transferred between the two modes of the motion, resulting in beats of period τ_B (of the q-w motion).

For the discussion of the angular momentum we distinguish between the case of L_3, which is a conserved quantity both in the quantal and TDVP time propagation, and L^2, which is not conserved under the TDVP dynamics. In figure 5 we show L_3 together with its dispersion $\Delta L_3 = [L_3^2 - \langle\phi|\mathbf{L}_3^2|\phi\rangle]^{1/2}$ for the TDVP motion. L_3 is a constant of the motion equal to the conserved quantal expectation value of $\mathbf{L}_3$. The dispersion

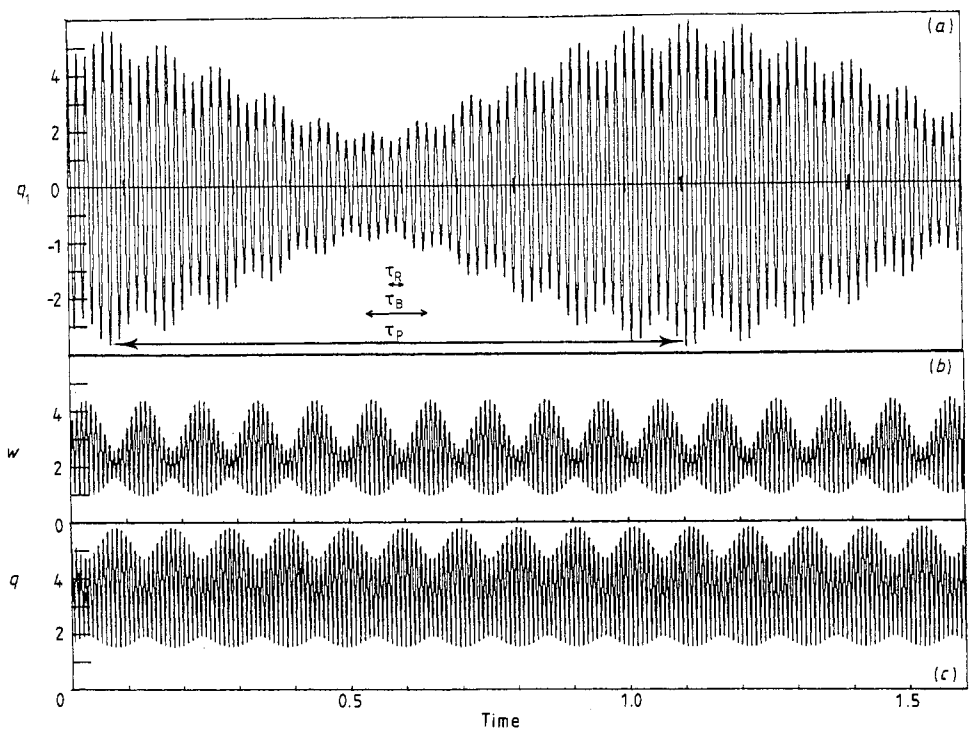

Figure 2. Time evolution of parameter (*a*) q_1, (*b*) w and (*c*) q, all in 10^{-11} m with initial conditions as in text, and time in ps.

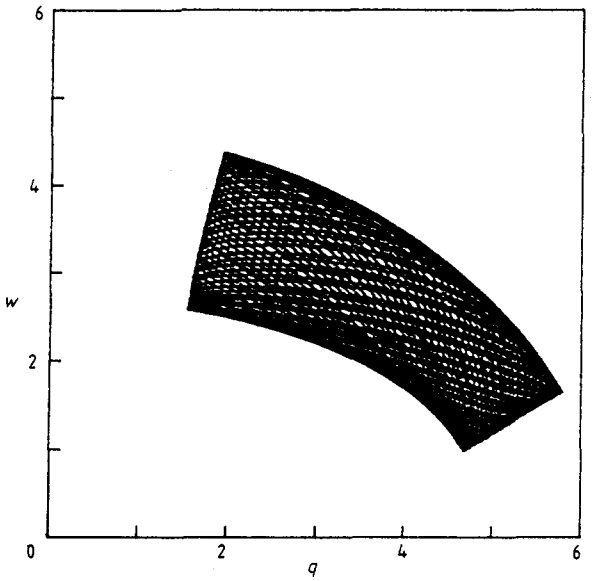

Figure 3. TDVP trajectory (initial conditions given in text) of the (q, w) parameters in units of 10^{-11} m.

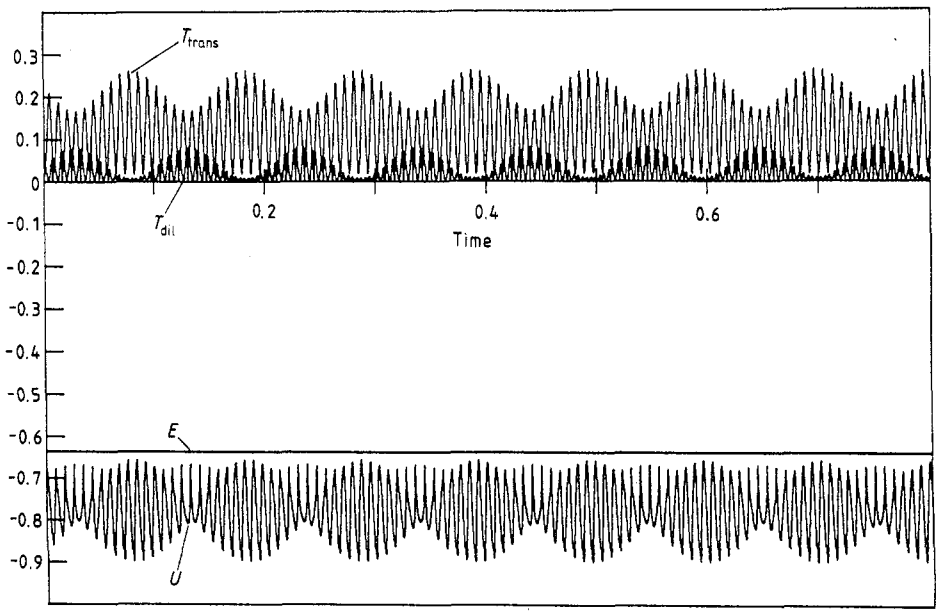

Figure 4. Time evolution of the WP energy E, and its constituent terms, i.e. potential energy U, translational kinetic energy T_{trans} and dilational kinetic energy T_{dil}. Units are 10^{-18} Joule for energy and ps for time.

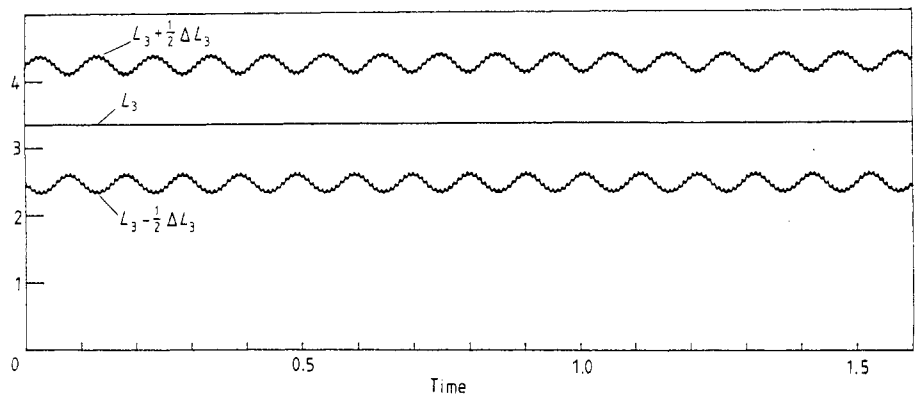

Figure 5. TDVP time evolution (initial conditions given in text) of L_3 and ΔL_3 in units $\hbar$; time is in ps.

ΔL_3 oscillates with the beat period τ_B and radial period τ_R and an amplitude small with respect to the mean value.

In figure 6 we plot L^2. Whereas L^2_{Quantum} is conserved, L^2_{TDVP} fluctuates between two extreme values $L^2_{\min}$ and $L^2_{\max}$. As far as the comparison between quantum and TDVP is concerned, it should be pointed out that there is an arbitrariness due to the choice of initial conditions. Indeed, at each moment of time the WP can be considered as an initial wavefunction for which the quantal evolution can be compared with the TDVP evolution. Hence by adapting the initial conditions we can keep the phase space trajectory, and in particular L^2 and L_3, the same and have for L^2_{Quantum} any value between $L^2_{\min}$ and $L^2_{\max}$. Any meaningful comparison between the (classical) TDVP and the quantum value for the L^2 would therefore require some sort of averaging over the TDVP trajectory.

As a conclusion concerning the conservation laws, we can state that the TDVP approximation reproduces the energy and the third component of angular momentum correctly and that the conservation of L^2 is violated over a period of the order of τ_B by an amount of at least $\frac{1}{2}(L^2_{\max}-L^2_{\min})$.

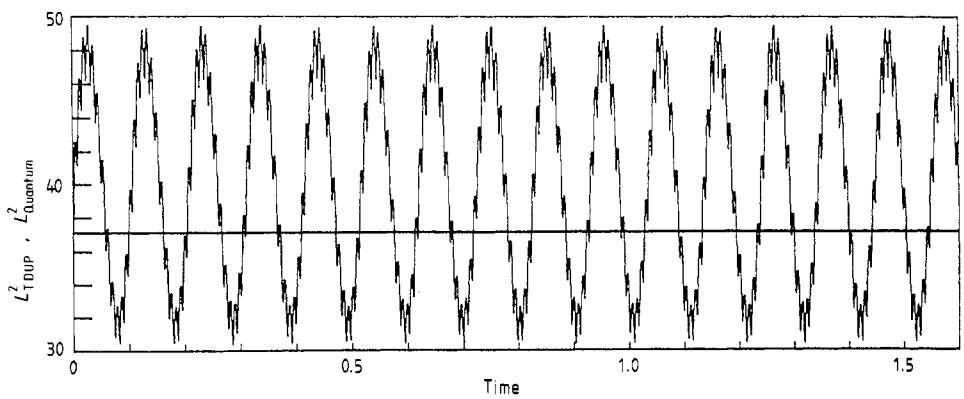

Figure 6. Time evolution (initial conditions given in text) of L^2_{TDVP} (oscillatory curve) and L^2_{Quantum} (straight line), both in units $\hbar^2$, time is in ps.

6. Conclusions

We have investigated the equivalence of the time-dependent variational principles in current use for the approximate time propagation of parametrised wavefunctions or wavepackets. Equivalence is found to occur whenever one has pairs of complementary parameters in the wavefunctions. This applies in particular to the Gaussian wavepackets that are frequently used in molecular physics problems.

Since the dynamics generated by the variational principles differs from the exact quantal one, the associated time evolution of physical quantities is not expected to coincide either. In particular, conservation laws may be violated. A study effected using the Hamilton-like TDVP formalism reveals that under certain conditions a quantity may be both quantally and TDVP conserved. These conditions are formulated in the group theoretic framework for the construction of the parametrised wavepackets.

The TDVP applied to a N-dimensional spherical Gaussian WP and a Hamiltonian composed of kinetic energy and a local potential was shown to lead to a set of classical Hamilton-like equations for the time evolution of the centre, translational momentum, width and dilational momentum. For a rotationally invariant potential, angular momentum operators are seen to be interesting candidates for a study of conservation laws in the TDVP.

A numerical illustration for the spherical Gaussian well was worked out. The parameter trajectories were analysed and their quasi-periodicity characterised by distinctive timescales. Our studies show that intrinsic conservation laws (energy and angular momentum components) are numerically fulfilled to a high degree of accuracy, but that in case of a TDVP breakdown of a quantal conservation law great care has to be taken in the interpretation of the results.

Acknowledgments

L Lathouwers would like to acknowledge support from the NFWO Belgium, the NATO Scientific Affairs Division (grant 84-716) and the NSF (grant CHE 8417571).

Appendix

In § 3 we consider a group theoretic operator method for the construction of the parametrised TDVP states, i.e.

$$\phi(x|\alpha) = \exp\left(\mathrm{i}\sum \alpha_m \mathbf{A}_m\right)\phi(x|0) \tag{A1}$$

where the $\{\mathbf{A}_m\}$ are a Lie algebra and $\phi(x|0)$ is a suitably chosen reference state. This is actually Perelomov's method of defining generalised coherent states for an arbitrary Lie group G. For more information we refer to the literature [13].

The Gaussian wavepackets (GWP) of (31) in § 4 of the text can be constructed as above, using the operators (where $\bar{\mathbf{x}}$, $\bar{\mathbf{p}}$ and $\bar{\mathbf{L}}$ are N-dimensional vectors, N being the number of coordinates in $\phi(x\gamma 0)$)

$$\{\mathbf{A}_m\} = \{\mathbf{Id}, \bar{\mathbf{x}}, \bar{\mathbf{p}}\} \oplus \{\{\bar{\mathbf{x}}\cdot\bar{\mathbf{x}}, \bar{\mathbf{x}}\cdot\bar{\mathbf{p}} + \bar{\mathbf{p}}\cdot\bar{\mathbf{x}}, \bar{\mathbf{p}}\cdot\bar{\mathbf{p}}\} \oplus \bar{\mathbf{L}}\} \tag{A2}$$

and the reference state

$$\phi(x|0) = \exp\left(-\sum_j x_j^2/2\right). \tag{A3}$$

Three algebras are involved, namely the Heisenberg-Weyl algebra W(N) for N dimensions, the symplectic algebra sp(2, $\mathbb{R}$) and the angular momentum algebra so(3). They give rise to a Lie group with the semi-direct product structure [14, 15]:

$$G = W(N) \oplus (Sp(2, \mathbb{R}) \otimes SO(3)).$$

In the operator action (A1) on (A3), the subgroup H of G generated by $\{\mathbf{Id}, (\bar{\mathbf{x}}^2 + \bar{\mathbf{p}}^2), \bar{\mathbf{L}}\}$ may be discarded because it only produces a phase factor. H is the so-called stability group of the reference state $\phi(x|0)$ under the group action. Thus one needs to consider in equation (A1) group elements representing the cosets of G/H. With a little effort [14, 16] one shows that these elments can be written in product form:

$$\prod_j [\exp(ip_j\mathbf{x}_j)\exp(-iq_j\mathbf{p}_j)] \exp\left(i\frac{Nu}{2w}\sum_j \mathbf{x}_j^2\right) \exp\left[-i\ln\left(\frac{2w^2}{N}\right)^{1/4} \sum_j (\mathbf{x}_j\mathbf{p}_j + \mathbf{p}_j\mathbf{x}_j)\right]. \tag{A4}$$

The effect on the reference state $\phi(x|0)$ is then easily evaluated. One recognises the translation of the WP centre to position (q_j) accompanied by a boost to linear momentum (p_j) and similarly a dilation to width w accompanied by a boost to scaling momentum u (cf above). This establishes the GWP as generalised coherent states for G/H and allows us to use the theory of § 3 in the analysis of conservation laws in GWP-TDVP dynamics.

References

[1] Broeckhove J, Lathouwers L and Van Leuven P (eds) 1986 *Proc. Int. Meeting on Dynamics of Wave Packets in Molecular and Nuclear Physics, Priorij Corsendonck, Belgium 1985* (*Lecture Notes in Physics* **256**) (Berlin: Springer)

[2] Dirac P A M 1930 *Proc. Cam. Phil. Soc.* **26** 376
Frenkel J 1934 *Wave Mechanics* (Oxford: Oxford University Press) p 435

[3] McLachlan A D 1964 *Mol. Phys.* **8** 39

[4] Heller E J 1976 *J. Chem. Phys.* **64** 63

[5] Kramer P and Saraceno M 1981 *Geometry of the Time-Dependent Variational Principle in Quantum Mechanics* (*Lecture Notes in Physics* **140**) (Berlin: Springer)

[6] Kerman A K and Koonin S E 1976 *Ann. Phys.* **100** 332

[7] Kucar J, Meyer H D and Cederbaum L S 1986 *Chem. Phys. Lett.* **128** 310

[8] Sawada S, Heather R, Jackson B and Metiu H 1985 *J. Chem. Phys.* **83** 3009

[9] Arickx F, Broeckhove J, Kesteloot E, Lathouwers L and Van Leuven P 1986 *Chem. Phys. Lett.* **128** 310

[10] Grad J, Yan Y J, Haque A and Mukamel S 1987 *J. Chem. Phys.* **86** 3441

[11] Singer K and Smith W 1986 *Mol. Phys.* **57** 761

[12] Broeckhove J, Lathouwers L and Van Leuven P 1989 *J. Mol. Struct. Theochem* (Special issue in honour of Professor P O Löwdin) in press

[13] Perelomov A 1986 *Generalized Coherent States and their Applications* (Berlin: Springer)

[14] Aldaya V, de Azcarraga J A and Wolf K B 1984 *J. Math. Phys.* **25** 506-12

[15] Haskell T G and Wybourne B G 1973 *Proc. R. Soc.* A **334** 541-51

[16] Gilmore R 1974 *Lie Groups, Lie Algebra's and some of Their Applications* (New York: Wiley)