© **2007** Nonlinear Phenomena in Complex Systems

Gaussian Wave Packet Dynamics in the Diamagnetic H-Atom

T. Fabčič, J. Main, and G. Wunner*
Insitut für Theoretische Physik 1, Universität Stuttgart, 70550 Stuttgart, GERMANY
(Received 17 March 2006)

The method of Gaussian wave packet (GWP) propagation introduced by Heller is a popular tool for doing time dependent quantum mechanical calculations in particular in molecular and nuclear physics. We show that this method is also applicable to atomic systems. We concentrate on the H-atom in a strong magnetic field, where a well-known regularization is used to remove the singularity. The Coulomb potential is transformed to a harmonic potential making GWP especially suitable. All equations of motion are obtained in analytic form. The matrix singularity problem encountered in the equations of motion derived from a time dependent variational principle is overcome by using a singular value decomposition (SVD).

PACS numbers: 31.15.Pf; 05.45.Mt
Keywords: Gaussian wave packets, variational approximation

1. Introduction

The idea of using time dependent GWP to approximate the evolution of some quantum mechanical wave function, introduced by Heller [1, 2], assumes a Gaussian form of the wave function for all times. The time dependence of the GWP is contained in the parameters like width, momentum, center and phase. Their time evolution is determined by first order differential equations obtained by a time dependent variational principle [3, 4, 7]. Of course the approximation of a wave function by a single GWP is poor for long time dynamics, except for harmonic potentials. It is therefore necessary to use a linear combination of GWP to achieve a better approximation of the exact wave function.

The method of GWP is mainly used in molecular and nuclear dynamics. It is, however, also possible to apply it to the H-atom in strong external fields. To this end it is advantageous to regularize the singulary Coulomb potential, which is done by a well-known transformation. The transformed Hamiltonian recommends the use of GWPs as trial functions since the Coulomb potential is transformed to a harmonic potential and the external fields just give higher-order terms.

In particular we apply the method of GWPs to a H-atom in a strong magnetic field, although we have to make a restriction up to now, discussed later.

In the course of integration, difficulties are encountered when the overlap matrix of the different coupled GWPs becomes numerically singular. This is caused by the overcompleteness of the basis of GWPs, where the number of coupled GWP is too large and one or more of the GWPs are redundant. This problem is known, and different ideas have been proposed to overcome the difficulties. Some authors advise to adjust the number of coupled GWP during integration, i.e. to increase the number of GWP when the wave function spreads, and to reduce it when the wave function shrinks [7, 8]. Another idea is to keep the number of basis functions constant and to regularize the matrix in the equations of motion for the parameters of the trial functions [5] using SVD [6] in the case of singularity. Here we adopt the latter method, which works well but has the drawback that the time steps of integration be-

*E-mail: fabcic@itp1.uni-stuttgart.de

come extremely small around the matrix singularities. It should be emphasized that the generically observed singularities of the overlap matrix in this system are only of numerical nature, i.e. its smallest eigenvalue does not approach zero, while the largest eigenvalue gets extremely large, making the matrix very ill-conditioned without being singular in a mathematical sense.

2. Regularization of the H-atom in an external magnetic field

GWP are exact solutions of harmonic potentials. It can therefore be assumed that the results obtained by the GWP dynamics are the better the smaller the deviation of the underlying potential from a harmonic potential is. To apply the method of GWP to the H-atom it is therefore useful to transform the singular Coulomb potential to a harmonic potential. Additional external fields yield additional higher order terms in the coordinates. Such a regularization is well known to be accomplished by introducing semiparabolic coordinates (μ, ν), a new time variable τ and the real scaling parameter n:

$$\begin{aligned} \mu &= \sqrt{n}\sqrt{r+z} \\ \nu &= \sqrt{n}\sqrt{r-z} \end{aligned}, \qquad \frac{d\tau}{dt} = 2r.$$

The regularized Hamiltonian H is then obtained as

$$\begin{aligned} H = &\frac{1}{2}(p_\mu^2 + p_\nu^2) + \alpha(\mu^2 + \nu^2) \\ &+ \frac{1}{8}\beta^2\mu^2\nu^2(\mu^2+\nu^2) = 2n, \end{aligned} \tag{1}$$

where $\alpha = -n^2 E$ and $\beta = n^2\gamma$. The eigenvalue problem $H\varphi_i = 2n_i\varphi_i$ gives the effective principal quantum number n_i, from which the eigenenergy and the magnetic field strength follow by

$$E_i = -\alpha/n_i^2, \quad \gamma_i = \beta/n_i^2.$$

Since GWP are exact solutions in harmonic potentials, we want our Hamiltonian (1) to be as harmonic as possible. It is obvious that H describes a 2-D harmonic oscillator perturbed by the diamagnetic term only if we assume the semiparabolic coordinates μ, ν to be cartesian. This is the case for the 2-D H-atom. For this reason we concentrate on the 2-D diamagnetic H-atom in this article, although we are confident an extension of this method to the 3-dimensional case is possible.

3. Equations of motion

The equations of motion derived from a time dependent variational principle for Gaussian trial functions [7] are summarized in this section for completeness. Consider a D-dimensional quantum system described by the Schrödinger equation $i\partial_t\psi(x,t) = \widehat{H}\psi(x,t)$, $x = (x_1, \ldots, x_D)$. A variationally optimal approximation to the exact wave function $\psi(x,t)$ is obtained from a trial function $\chi(z_t, x)$ whose time dependence is contained in the complex parameters $z_t = (z_t^1, \ldots, z_t^n)$ by the time dependent variational principle

$$\langle \delta\chi | i\partial_t - \widehat{H} | \chi \rangle = 0. \tag{2}$$

The variations are restricted by the functional form of $\chi(z_t, x)$. For the equations of motion of the parameters z_t we obtain

$$K\dot{z}_t = -ih, \tag{3}$$

with

$$K = \langle \partial\chi/\partial z_t | \partial\chi/\partial z_t \rangle, \quad h = \langle \partial\chi/\partial z_t | \widehat{H} | \chi \rangle. \tag{4}$$

In the regularized 2-D H-atom it is obvious that GWP are well suited as trial functions since the singular Coulomb potential has been transformed to a harmonic potential and the magnetic field gives terms of higher order. As trial functions for our calculations we use a sum of GWP

$$g(y_t^k, x) = \exp[i(x a_t^k x + b_t^k \cdot x + c_t^k)], \tag{5}$$

where a_t^k is a complex symmetric matrix, b_t^k is a complex vector and a complex number c_t^k, denoted collectively by y_t^k. Since we use a superposition of GWPs the trial function $\chi(z_t, x)$ can be

written as

$$\chi(z_t, x) = \sum_{k=1}^{N} g(y_t^k, x), \tag{6}$$

with $z_t = (y_t^1, \ldots, y_t^N)$. The equations of motion of the parameters follow from the variational principle (2):

$$\begin{aligned} \dot{a}_t^k &= -2(a_t^k)^2 - \frac{1}{2} v_{2,t}^k && (7)\\ \dot{b}_t^k &= -2a_t^k b_t^k - v_{1,t}^k && (8)\\ \dot{c}_t^k &= -\frac{1}{2}(b_t^k)^2 + i\mathrm{Tr}\, a_t^k - v_{0,t}^k. && (9) \end{aligned}$$

The complex symmetric matrix $v_{2,t}^k$, the complex vector $v_{1,t}^k$ and the complex number $v_{0,t}^k$ are obtained from the solution of the set of linear equations ($g(y_t^k, x) = g^k$ has been set):

$$\sum_{k=1}^{N} v_{0,t}^k \langle g^l | x_i^m x_j^n | g^k \rangle + \sum_{k=1}^{N} \langle g^l | x_i^m x_j^n x \cdot v_{1,t}^k | g^k \rangle + \frac{1}{2} \sum_{k=1}^{N} \langle g^l | x_i^m x_j^n x v_{2,t}^k x | g^k \rangle = \sum_{k=1}^{N} \langle g^l | x_i^m x_j^n V(x) | g^k \rangle, \tag{10}$$
$$l = 1, \ldots, N \quad m + n = 0, 1, 2 \quad i, j = 1, \ldots, D.$$

The potential $V(x)$ on the right-hand side remains of the Hamiltonian of the underlying system. The kinetic term of the Hamiltonian is already accounted for in (7),(8),(9). For numerical reasons we do not solve (7),(8) and (9) directly, but introduce the real, vector-valued functions

$$\begin{aligned} x_t^k &= -\tfrac{1}{2}\left(\mathrm{Im}\, a_t^k\right)^{-1} \mathrm{Im} b_t^k \\ p_t^k &= \mathrm{Re}\left(b_t^k + 2a_t^k x_t^k\right) \end{aligned}$$

and the complex phase and normalization parameters

$$\gamma_t^k = c_t^k + \frac{1}{2}\left(b_t^k + p_t^k\right) \cdot x_t^k. \tag{11}$$

With these new parameters x_t^k, p_t^k, γ_t^k and the matrix a_t^k, the exponent of the GWP (5) now reads $[i((x - x_t^k) a_t^k (x - x_t^k) + p_t^k \cdot (x - x_t^k) + \gamma_t 1^k)]$, where in the case of a single GWP ($N = 1$) x_t, p_t are just the expectation values of the momentum and the position operator, respectively. These new parameters are smooth function of time and allow for larger time steps in the integration algorithm.

The derivatives of the parameters x_t^k, p_t^k, γ_t^k are calculated from a_t^k, b_t^k, c_t^k and their derivatives

$$\begin{aligned} \dot{x}_t^k &= \xi^{-1}\left(-\dot{\xi}\xi^{-1}\mathrm{Im} b_t^k + \mathrm{Im}\dot{b}_t^k\right) \\ \dot{p}_t^k &= \mathrm{Re}\left(\dot{b}_t^k + 2\dot{a}_t^k x_t^k + 2a_t^k \dot{x}_t^k\right) && (12)\\ \dot{\gamma}_t^k &= \dot{c}_t^k + \frac{1}{2}\left(\dot{b}_t^k + \dot{p}_t^k\right) \cdot x_t^k + \frac{1}{2}\left(b_t^k + p_t^k\right) \cdot \dot{x}_t^k, \end{aligned}$$

where $\xi = -2\mathrm{Im} a_t^k$. Similarly it is advisable to introduce the complex matrices q_t^k, w_t^k according to $a_t^k = \frac{1}{2} q_t^k (w_t^k)^{-1}$ and to integrate the equations

$$\begin{aligned} \dot{w}_t^k &= q_t^k \\ \dot{q}_t^k &= -2v_{2,t}^k w_t^k \end{aligned} \tag{13}$$

instead of (7) which is very oscillating due to the $(a_t^k)^2$ term, and causes numerical difficulties during integration.

4. Integration of the equations of motion

There are good reasons to use many GWP in order to have many parameters to adjust and a great flexibility to make a good approximation to the exact wave function. On the other hand the use of many GWP often leads to numerical problems in integrating the equations of motion. As mentioned before it can happen from time to time in the course of integration, depending on how many coupled GWP are propagated, that the basis becomes numerically overcomplete and one or more GWP become redundant. This is the case when e.g. the norm of one single GWP is small while others become extremely large, or when two or more GWP strongly overlap and nearly coincide. In both cases the matrix S occurring in the system of linear equations (10) becomes ill-conditioned and cannot be numerically inverted in the worst case, although it has been shown that a solution of (10) exists even if the matrix S is singular [5].

If S is very ill-conditioned we make use of the SVD [6] of S, i.e. $S = U\Omega V^\dagger$, with unitary matrices U, V and a diagonal matrix $\Omega = \mathrm{diag}(\omega_j)$ with real non-negative singular values ω_j. Then the inverse S^{-1} is simply $S^{-1} = V\Omega^{-1}U^\dagger$ where $\Omega^{-1} = \mathrm{diag}(1/\omega_j)$. Inverse values $(1/\omega_j)$ are set to zero for all ω_j smaller than some threshold ϵ [6]. We used a relative threshold $\epsilon = 3.0 \times 10^{-14}\omega_{\max}$ since the condition number $\omega_{\max}/\omega_{\min}$ gives information about how well or ill-conditioned the matrix is.

Such a numerical matrix singularity in the course of integration is presented in figure 1 where some significant parameters are plotted as functions of time, obtained from four coupled GWP propagated by (13) and (12) using the Hamiltonian (1) with $\alpha = 0.5$ and $\beta = 0.2$. The dotted line in figure 1a shows the CPU-time needed for integration of intervals $\Delta\tau$ in arbitrary units. Obviously there are two dramatic slow-downs of the integration velocity at about $\tau/\tau_{cl} \approx 5.4$ and $\tau/\tau_{cl} \approx 5.7$ (τ_{cl} is the classical period of small oscillations) due to decreasing time steps of the integration routine. The tiny integration time steps are caused by the ill-conditioned, near-singular matrix S around these two points. The (ir)regularity of S is determined from the ratio of its minimum and maximum singular values, both plotted with solid lines in figure 1a. Obviously the condition number is numerically close to infinity, indicating a numerically almost singular matrix. In this example the near-matrix singularity is produced mainly by the large difference of norms of the four coupled GWP (the 'smallest' and the 'biggest' GWPs are plotted with dashed lines) giving matrix elements S_{ij} varying widely in magnitude. It is only to a lesser degree produced by overlapping GWPs. This can be concluded from the eigenvalues of the overlap matrix of the GWPs $\langle g^k|g^l\rangle$, see figure 1b. Even the smallest eigenvalue $\lambda_{\min}$ is far from zero in the region of near numerical singularity ($\lambda_{\min} > 0.01$) which would be exactly zero in case of two exactly coinciding GWP.

In this example, monitoring the smallest eigenvalues of the overlap matrix to detect numerical problems [7, 8] would fail, although this is a very common kind of numerical matrix singularity encountered in this system. A better test would be here to observe the ratio of the minimal to the maximal eigenvalue.

We want to mention that the norm of the variationally propagated wave functions is of course conserved (see e.g. [9]). Nevertheless some of the coupled GWPs can become very large (figure 1a) but partially cancel out each other. We note that this example of an ill-conditioned matrix in the course of integration shown in figure 1 is not a very severe one and integration would be possible even without regularization using SVD, but of course there are worse cases where SVD is necessary to succeed with the matrix inversion and integration. Although the method of using SVD guarantees a successful integration a drawback of this method are still the extremely small time steps of the integration algorithm (we use Adams and Runge-Kutta routines) when the ma-

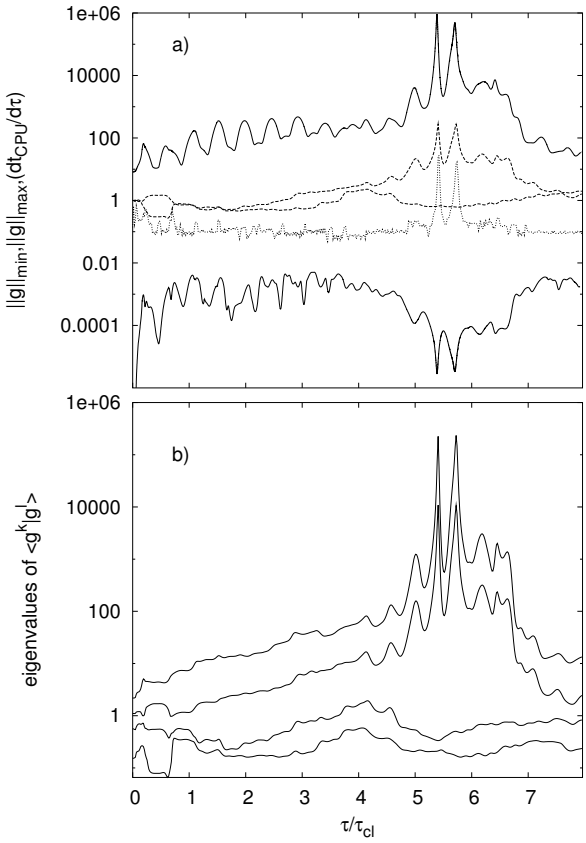

FIG. 1. a) Norm of two single GWP (dashed), the smallest and largest singular values (solid) and the reverse velocity of integration ($\Delta t_{\mathrm{CPU}}/\Delta\tau$) (dotted) as functions of the integration time τ. In b) the eigenvalues of the overlap matrix $\langle g^k|g^l\rangle$ of the coupled GWPs are shown. For details read the text.

trix S is singular. The procedure using SVD to regularize S is based on that of Kay [5] where a similar regularization is applied directly to K in (3) for arbitrary trial functions and applied on one-dimensional trial functions. The approach in this article could be seen as an adjusted application of Kay's method of regularization on GWPs as trial functions.

5. Numerical results

The accuracy of the GWP method is tested by comparison of data obtained by the GWP method and by numerically exact propagation. In particular, we investigate the autocorrelation function $C(\tau) = \langle\chi(z_\tau)|\chi(z_0)\rangle$ plotted in figure 2. All eight initial GWP are chosen to be centered at the origin with a diagonal width matrix $a_0^k = 0.18\times\mathbf{1}$, and have the same phase and norm. Their initial momenta p_0^k all have the same magnitude $(p_0^k)_\mu^2 + (p_0^k)_\nu^2$ and are equally spaced between the directions parallel and perpendicular to the magnetic field. This choice ensures that the classical motion of these initial phase space points would reach different regions of the classically available phase space, but is of course not optimal with respect to a fast integration, because the initial GWP do strongly overlap. However here we are not as much interested in an optimal (with respect to a fast integration) initial choice of the wave function as we are in the regularization of the Matrix S using SVD and its numerical applicability. The agreement between the autocorrelation function $C(\tau)$ obtained by the method of GWPs and obtained by numerical exact calculation is very good for about 10 classical periods as can be seen in figure 2.

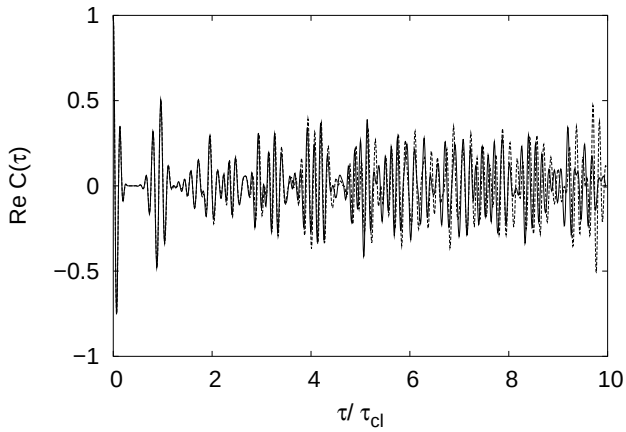

FIG. 2. Real part of the autocorrelation function $\langle\chi(z_t)|\chi(z_0)\rangle$. The initial values of the eight coupled GWPs are given in the text. The autocorrelation function obtained by the method of GWP dynamics is plotted with solid line and is compared to numerical exact calculation, plotted with dashed line.

In summary, we have shown that propagation of coupled GWP is possible without changing its number, if a SVD is used when the ma-

trix in the equations of motion is singular. However a severe practical drawback is that the time steps of integration become extremely small during singularities, rendering the process of integration very slow. This fact might favor other methods to overcome the matrix singularity problem, although they have their own disadvantages. For the regularized 2-D diamagnetic H-Atom good results are obtained using coupled GWPs, and an extension to three dimensions is now desirable.

References

[1] E.J Heller. J. Chem. Phys. **62**, 1544-1554 (1975).
[2] E.J Heller. J. Chem. Phys. **64**, 63-73 (1976).
[3] P.A.M. Dirac. Proc. Cam. Phil. Soc. **26**, 376-385 (1930).
[4] A.D. McLachlan. Mol. Phys. **8**, 39-44 (1964).
[5] K.G. Kay. Chem. Phys. **137**, 165-175 (1989).
[6] W.H. Press, S.A. Teukolsky, W.T. Vetterling, B.P. Flannery. *Numerical Recipes* (University Press, Cambridge, 1992).
[7] S.-I. Sawada, R. Heather et al. J. Chem. Phys. **83**, 3009-3027 (1985).
[8] R. Heather, H. Metiu. J. Chem. Phys. **84**, 3250-3259 (1986).
[9] R.D. Coalson, M. Karplus. J. Chem. Phys. **93**, 3919-3930 (1990).