

ON VARIATIONAL APPROXIMATIONS IN QUANTUM MOLECULAR DYNAMICS

CHRISTIAN LUBICH

ABSTRACT. The Dirac-Frenkel-McLachlan variational principle is the basic tool for obtaining computationally accessible approximations in quantum molecular dynamics. It determines equations of motion for an approximate time-dependent wave function on an approximation manifold of reduced dimension. This paper gives a near-optimality result for variational approximations. It bounds the error in terms of the distance of the exact wave function to the approximation manifold and identifies the parameters that control the deviation of the variational approximation from the best approximation on the manifold.

1. INTRODUCTION

For dealing with atoms involving many electrons the accurate quantum theory, involving a solution of the wave equation in many-dimensional space, is far too complicated to be practicable. One must therefore resort to approximate methods.

(P.A.M. Dirac 1930, in [6])

Computations in quantum molecular dynamics rely on approximations that are based on a variational principle due to Dirac (later restated by Frenkel and McLachlan). This variational principle restricts the approximate time-dependent wave function to a manifold of admissible configurations, which is chosen so that the high dimensionality of the problem is substantially reduced and a computational treatment becomes feasible. We recapitulate the Dirac-Frenkel-McLachlan variational principle in Section 2 and describe typical approximations obtained from it (adiabatic approximation, time-dependent Hartree and Hartree-Fock methods, Gaussian wave packets) in Section 3.

Despite the fundamental role and widespread use of this variational principle, it seems that no error analysis has been given in the literature. Much work has been done on asymptotic problems (adiabatic perturbation theory and semiclassical analysis, e.g. [11, 15]), but apparently not on the quality of the variational approximation. Here we study the following question: *If the wave function is close to the manifold, does the variational principle then provide a good approximation?* The closeness of the exact wave function to the chosen approximation manifold is a modeling hypothesis which may or may not be satisfied in a given problem. If it is a viable hypothesis one would, however, hope that the variational principle,

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which establishes approximate equations of motion on the manifold, yields an approximate wave function that is close to the best approximation to the true wave function on the manifold. This is a familiar question in other areas of numerical analysis; cf. Céa's lemma on the optimality of Galerkin approximations of elliptic boundary value problems [5, p. 113].

In Section 4 we give a near-optimality result for the variational approximation in the situation of bounded coupling potentials. The error bound exhibits the parameters that control the deviation of the variational approximation from optimality: the length of the time interval, bounds for the nonseparable part of the Hamiltonian, the curvature of the manifold, and the regularity of the wave function. In Section 5 we derive an error bound for the case of (unbounded) Coulomb potentials, where closeness of the wave function to the approximation manifold is required in a stronger norm than the L^2 norm of the error bound.

2. THE DIRAC-FRENKEL-McLACHLAN VARIATIONAL PRINCIPLE

2.1. The variational principle. The abstract setting is that of the time-dependent Schrödinger equation

$$(2.1) \quad i \frac{d\psi}{dt} = H\psi, \quad \psi(0) = \psi_0$$

where the Hamiltonian H is a self-adjoint linear operator on a complex Hilbert space \mathcal{H} with inner product $\langle \cdot, \cdot \rangle$ and norm $\| \cdot \|$. Let $\mathcal{M} \subset \mathcal{H}$ be a manifold on which an approximation to the wave function $\psi(t)$ should lie, and let $T_u\mathcal{M}$ denote the tangent space at $u \in \mathcal{M}$ (i.e., the closed real-linear subspace of \mathcal{H} formed of the derivatives of all paths on \mathcal{M} passing through u , or in physical terminology, the space of admissible variations). The variational principle as formulated by Frenkel [7, p. 253]¹ and McLachlan [12] determines the approximate wave function $t \mapsto u(t) \in \mathcal{M}$ from the condition that the time derivative should satisfy, at every time t ,

$$(2.2) \quad \frac{du}{dt} = \theta \in T_{u(t)}\mathcal{M} \quad \text{with} \quad \left\| \theta - \frac{1}{i}Hu(t) \right\| = \min !$$

This amounts to projecting the vector field at u to the tangent space at u ,

$$(2.3) \quad \frac{du}{dt} = P(u) \frac{1}{i}Hu$$

with the orthogonal projection $P(u) : \mathcal{H} \rightarrow T_u\mathcal{M}$ given by $\operatorname{Re} \langle \delta u, P(u)\varphi \rangle = \operatorname{Re} \langle \delta u, \varphi \rangle$ for all $\delta u \in T_u\mathcal{M}$ and $\varphi \in \mathcal{H}$. Equivalently,

$$(2.4) \quad \operatorname{Re} \left\langle \delta u, \frac{du}{dt} - \frac{1}{i}Hu \right\rangle = 0 \quad \text{for all } \delta u \in T_u\mathcal{M},$$

which in numerical analysis would be called a Galerkin condition. The variational principle used by Dirac [6] and Frenkel [7, p. 253 and p. 435 f.] is the above condition without taking the real part, which is equivalent if $T_u\mathcal{M}$ is a *complex* linear space. In that case, choosing $\delta u = i du/dt$ shows that the total energy $\langle u, Hu \rangle$ is conserved along solutions of (2.4). If $u \in T_u\mathcal{M}$ for all $u \in \mathcal{M}$, which is the case if with $u \in \mathcal{M}$ also real multiples of u are in \mathcal{M} , then the choice $\delta u = u$ yields the conservation of the norm $\|u\|$ along solutions of (2.4); see also [3, App. A].

¹ Frenkel refers to Dirac: "The argument presented below is taken from Dirac's appendix to the Russian edition of his book, *The Principles of Quantum Mechanics*." [7, p. 253]

2.2. An a posteriori error bound. A very simple but useful bound is

$$(2.5) \quad \|u(t) - \psi(t)\| \leq \int_0^t \text{dist}(iHu(s), T_{u(s)}\mathcal{M}) ds ,$$

which holds if $u(0) = \psi(0) \in \mathcal{M}$; cf. [14] for an attempt towards an estimate of this type. The bound (2.5) is obtained by subtracting (2.1) from (2.3), so that $\frac{d}{dt}(u - \psi) = -iH(u - \psi) + Q(u)iHu$ with $Q(u) = I - P(u)$, and by multiplying with $u - \psi$ and taking the real part. This gives

$$\begin{aligned} \|u - \psi\| \cdot \frac{d}{dt} \|u - \psi\| &= \frac{1}{2} \frac{d}{dt} \|u - \psi\|^2 = \text{Re} \langle u - \psi, \frac{d}{dt}(u - \psi) \rangle \\ &= \text{Re} \langle u - \psi, Q(u)iHu \rangle \leq \|u - \psi\| \cdot \|Q(u)iHu\| . \end{aligned}$$

The error bound (2.5) now follows upon integrating and noting that

$$\text{dist}(iHu, T_u\mathcal{M}) = \|Q(u)iHu\| = \|i \frac{du}{dt} - Hu\| .$$

In this paper we concentrate on bounding the error in the norm $\|\cdot\|$ of the Hilbert space \mathcal{H} . For observables we just note the error bound, for any self-adjoint linear operator S ,

$$|\langle u, Su \rangle - \langle \psi, S\psi \rangle| = |\langle u - \psi, Su \rangle + \langle S\psi, u - \psi \rangle| \leq \|u - \psi\| \cdot (\|Su\| + \|S\psi\|).$$

2.3. The variational principle for time-dependent manifolds. The variational principle extends to time-dependent approximation manifolds \mathcal{M}_t . Suppose that \mathcal{M}_t is locally given by a differentiable parametrization $u = \chi(t, z) \in \mathcal{M}_t$, where z varies in a time-independent space. Then the time derivative of any path $t \mapsto u(t) \in \mathcal{M}_t$ is such that, at $u = u(t)$ for any fixed t ,

$$(2.6) \quad \frac{du}{dt} - s(t, u) \in T_u\mathcal{M}_t ,$$

where $s(t, u) = (\partial\chi/\partial t)(t, z)$ for $u = \chi(t, z)$. The variational principle therefore determines the approximate wave function $u(t) \in \mathcal{M}_t$ from the condition that the time derivative satisfy at every time t , for $u = u(t)$,

$$(2.7) \quad \frac{du}{dt} - s(t, u) = \theta \in T_u\mathcal{M}_t \quad \text{with} \quad \|\theta + s(t, u) - \frac{1}{i}Hu\| = \min!$$

Equivalently,

$$(2.8) \quad \frac{du}{dt} - s(t, u) = P(t, u) \left(\frac{1}{i}Hu - s(t, u) \right)$$

with the orthogonal projection $P(t, u) : \mathcal{H} \rightarrow T_u\mathcal{M}_t$. This equation is again equivalent to (2.4), now taken together with the condition (2.6). The integrand of the *a posteriori* error bound becomes

$$\text{dist}(\frac{1}{i}Hu - s(t, u), T_u\mathcal{M}_t) = \|Q(t, u)(\frac{1}{i}Hu - s(t, u))\| = \|i \frac{du}{dt} - Hu\| .$$

3. EXAMPLES OF VARIATIONAL APPROXIMATION

We list a few variational approximations that are widely used in chemical physics, ranging between the full molecular time-dependent Schrödinger equation and classical molecular dynamics.

3.1. Adiabatic approximation (e.g., [13, Chs. XVII, XVIII]). The state of a molecule consisting of n nuclei (with masses M_k and positions x_k) and ℓ electrons (with mass m and positions y_j) is described by a wave function

$$\Psi = \Psi(x_1, \dots, x_n, y_1, \dots, y_\ell, t)$$

(ignoring spin for the sake of simplicity), which is a solution of the *molecular Schrödinger equation* (in atomic units, $\hbar = 1$)

$$(3.1) \quad i \frac{\partial \Psi}{\partial t} = H_{\text{mol}} \Psi \quad \text{with} \quad H_{\text{mol}} = T_N + T_e + U ,$$

where T_N and T_e are the kinetic energy operators of the nuclei and electrons, respectively,

$$(3.2) \quad T_N = - \sum_{k=1}^n \frac{1}{2M_k} \Delta_{x_k} , \quad T_e = - \sum_{j=1}^{\ell} \frac{1}{2m} \Delta_{y_j} ,$$

and the potential $U = U(x, y) = U(x_1, \dots, x_n, y_1, \dots, y_\ell)$ is the sum of the Coulomb interactions of each pair of particles in the system. In a first step we ignore the contribution from the kinetic energy T_N of the nuclei (motivated by the fact that $M_k \gg m$), and consider the electronic Hamiltonian

$$H_e(x) = T_e + U(x, \cdot)$$

which acts on functions of the electronic coordinates y and depends parametrically on the nuclear coordinates x . Fix an eigenfunction $\Phi(x, \cdot)$ of $H_e(x)$ corresponding to the eigenvalue $E(x)$,

$$H_e(x)\Phi(x, \cdot) = E(x)\Phi(x, \cdot) ,$$

which depends continuously on x , is real-valued and of unit L^2 norm with respect to the y -variables. For fixed nuclear coordinates x , the solution of the *electronic Schrödinger equation*

$$(3.3) \quad i \frac{\partial \Psi_e}{\partial t} = H_e(x) \Psi_e$$

with initial value $\psi_0(x)\Phi(x, \cdot)$ is given by

$$\Psi_e(x, y, t) = e^{-iE(x)t} \psi_0(x) \cdot \Phi(x, y) .$$

This motivates the *adiabatic* or time-dependent *Born-Oppenheimer* approximation of (3.1), which is the variational approximation on

$$(3.4) \quad \mathcal{M} = \{u \in L^2_{x,y} : u(x, y) = \psi(x)\Phi(x, y), \psi \in L^2_x\} .$$

Note that here \mathcal{M} is a linear space so that $T_u \mathcal{M} = \mathcal{M}$ for all $u \in \mathcal{M}$. The Dirac-Frenkel-McLachlan variational principle (2.2) or (2.4) then leads, after a short calculation, to the *nuclear Schrödinger equation* on the electronic energy band E ,

$$(3.5) \quad i \frac{\partial \psi}{\partial t} = H_N \psi \quad \text{with} \quad H_N = T_N + E + \sum_{k=1}^n \frac{1}{2M_k} \|\nabla_{x_k} \Phi\|_{L^2_y}^2 ,$$

where H_N acts on functions of only the nuclear coordinates x , with E and the last term in (3.5) as the potential.

It is interesting to see what the error bound (2.5) yields in this situation. Since for $u(x, y) = \psi(x)\Phi(x, y)$ we have

$$T_N u = - \sum_{k=1}^n \frac{1}{2M_k} \left(\Delta_{x_k} \psi \cdot \Phi + 2 \nabla_{x_k} \psi \cdot \nabla_{x_k} \Phi + \psi \cdot \Delta_{x_k} \Phi \right),$$

(note that the first term in the bracket is in \mathcal{M}), we obtain

$$\text{dist}(iH_{\text{mol}} u, T_u \mathcal{M}) = \text{dist}(iT_N u, \mathcal{M}) \leq \sum_{k=1}^n \frac{1}{2M_k} \left\| 2 \nabla_{x_k} \psi \cdot \nabla_{x_k} \Phi + \psi \cdot \Delta_{x_k} \Phi \right\|_{L^2_{x,y}}.$$

In view of (2.5), the approximation can become poor only if the electronic eigenfunction $\Phi(x, y)$ has large derivatives with respect to x in a region where ψ is not negligible. This is the case near eigenvalue crossings or almost-crossings, where indeed the adiabatic approximation is known to break down.² The remedy then is to enlarge the approximation space by including several energy bands which are well separated from the remaining ones in the region of physical interest, e.g., using

$$\mathcal{M} = \{u \in L^2_{x,y} : u(x, y) = \psi_1(x)\Phi_1(x, y) + \psi_2(x)\Phi_2(x, y), \psi_1, \psi_2 \in L^2_x\},$$

where $\Phi_1(x, \cdot), \Phi_2(x, \cdot)$ span an invariant subspace of the electronic Hamiltonian $H_e(x)$. The variational approximation on \mathcal{M} then leads to a system of coupled Schrödinger equations for ψ_1, ψ_2 ; see, e.g., the contributions in [2].

3.2. Time-dependent Hartree and Hartree-Fock approximations [6, 12, 8, 3]. Consider the Schrödinger equation for the nuclei,

$$(3.6) \quad i \frac{\partial \psi}{\partial t} = H \psi \quad \text{with} \quad H = T_N + V,$$

with the kinetic energy operator (3.2) of the nuclei, $T_N = T_1 + \dots + T_n$, and a potential $V = V(x_1, \dots, x_n)$ (supposedly an approximation to the potential in (3.5)). In the case of a separable potential $V = V_1(x_1) + \dots + V_n(x_n)$ the equation has solutions of the product form

$$\psi(x, t) = \phi_1(x_1, t) \cdot \dots \cdot \phi_n(x_n, t)$$

for any initial value of this form, where the single-particle functions ϕ_k are solutions of decoupled Schrödinger equations

$$(3.7) \quad i \frac{\partial \phi_k}{\partial t} = (T_k + V_k) \phi_k.$$

For a nonseparable potential, the time-dependent *Hartree* or *self-consistent field* method is the variational approximation on

$$(3.8) \quad \mathcal{M} = \{u : u(x) = \phi_1(x_1) \cdot \dots \cdot \phi_n(x_n), \phi_k \in L^2_{x_k}\}.$$

Since \mathcal{M} is not a linear space, the variational principle here leads to nonlinearly coupled equations, which up to a phase factor are formally of the type (3.7) with

$$(3.9) \quad V_k = \left\langle \prod_{j \neq k} \phi_j, V \prod_{j \neq k} \phi_j \right\rangle.$$

Here the L^2 inner product is taken over all variables with the exception of x_k ; that is, V_k is the mean field potential obtained by averaging over the coordinates of all

²The critical term is $\Delta_{x_k} \Phi(x, \cdot)$, whose norm in L^2_y generically grows as $\sim \delta^{-2}$ if $E(x)$ comes δ -close to another eigenvalue of $H_e(x)$. Of essentially the same size and asymptotic behaviour is the last term in (3.5), which is usually neglected in computations.

other particles. A better approximation is usually obtained by allowing for a linear combination of Hartree products in the approximation,

$$(3.10) \quad \mathcal{M} = \{u : u(x) = \sum_J a_J \phi_{j_1}^{(1)}(x_1) \cdots \phi_{j_n}^{(n)}(x_n), \quad a_J \in \mathbf{C}, \quad \phi_j^{(k)} \in L^2_{x_k}\},$$

where the sum is over multi-indices $J = (j_1, \dots, j_n)$ with $1 \leq j_k \leq N_k$. This leads to the *multiconfiguration time-dependent Hartree* (MCTDH) method [3].

For the treatment of the electronic Schrödinger equation (3.3), where all particles are identical and indistinguishable, one must in addition take care of the antisymmetry of the wave function with respect to exchanging the coordinates (and spin) of any two particles, as is required by the Pauli principle. The variational approximation is therefore built on antisymmetrized products of single-particle functions (Slater determinants),

$$(3.11) \quad \mathcal{M} = \{u : u(y) = \det(\varphi_i(y_j))_{i,j=1}^\ell, \quad \varphi_i \in L^2\}.$$

The variational approximation of the electronic Schrödinger equation (3.3) on \mathcal{M} is known as the time-dependent *Hartree-Fock* method. It is actually the approximation considered by Dirac in [6].

3.3. Gaussian wave packets ([8] and, e.g., [1, Ch. 10]). Further computational simplification in the treatment of the Schrödinger equation for the nuclei is obtained if in the framework of the Hartree approximation, the functions ϕ_k are chosen in a parameterized form. Since for strongly localized wave packets the effective potential can be considered approximately quadratic and since Gaussian wave packets remain Gaussians in a quadratic potential, the choice is

$$\phi_k(x_k) = \exp\left(i\left((x_k - q_k)^* A_k (x_k - q_k) + p_k \cdot (x_k - q_k) + b_k\right)\right)$$

with real vectors q_k and p_k and complex parameters A_k (a matrix or, more usually, a scalar) and b_k . Here the variational approximation leads to classical-looking equations of motion for the positions q_k and momenta p_k ,

$$\dot{q}_k = \frac{p_k}{M_k}, \quad \dot{p}_k = -\langle \phi_k, \nabla_{x_k} V_k \phi_k \rangle$$

with the pre-averaged potential V_k of (3.9), and to differential equations for the width parameters A_k and phases b_k .

3.4. Quantum dressed classical mechanics [4]. Even if the approximation by a Gaussian wave packet is too rough, it can nevertheless be used in a correction scheme, which is once more based on the variational principle. Let $q_k(t)$, $p_k(t)$, $A_k(t)$, $b_k(t)$ be defined by Gaussian wave packet dynamics as in the previous subsection, possibly even further simplified by using the classical equations of motion $\dot{q}_k = p_k/M_k$, $\dot{p}_k = -\nabla_{q_k} V(q)$ and an analogous simplification in the differential equations for A_k and b_k . The variational approximation for (3.6) can then be based on the *time-dependent* approximation manifold (here actually a linear space)

$$(3.12) \quad \mathcal{M}_t = \{u : u(x_1, \dots, x_n) = \sum_J c_J \gamma_{j_1}^{(1)}(x_1, t) \cdots \gamma_{j_n}^{(n)}(x_n, t), \quad c_J \in \mathbf{C}\}.$$

The sum is over multi-indices $J = (j_1, \dots, j_n)$ with $0 \leq j_k \leq N_k$, and the functions $\gamma_j^{(k)}$ are shifted and scaled Gauss-Hermite basis functions defined by (we assume

all the x_i are one-dimensional for simplicity)

$$\gamma_j^{(k)}(x_k, t) = \exp\left(i\left(A_k(t)(x_k - q_k(t))^2 + p_k(t)(x_k - q_k(t)) + b_k(t)\right)\right) \cdot H_j\left(\sqrt{2\operatorname{Im} A_k(t)}(x_k - q_k(t))\right)$$

with Hermite polynomials H_j . This leads to a method which adapts the location and width of the basis functions to Gaussian wave packets that follow classical trajectories.

4. NEAR-OPTIMALITY OF THE VARIATIONAL APPROXIMATION

We bound the error of the variational approximation in terms of the best-approximation error $\operatorname{dist}(\psi(t), \mathcal{M})$ under assumptions that include, in the situation of a bounded coupling potential, the (multiconfiguration) time-dependent Hartree method and the approximation by Gaussian wave packets, as well as its refinement with time-dependent Gauss-Hermite basis functions.

4.1. Assumptions. In the abstract setting of Section 2 the Hamiltonian is split as

$$(4.1) \quad H = A + B$$

with self-adjoint linear operators A and B , where A corresponds to the separable part: $u \in \mathcal{M}$ implies $e^{-itA}u \in \mathcal{M}$ for all t . This is satisfied if and only if

$$(4.2) \quad iAu \in T_u\mathcal{M} \quad \text{for all } u \in \mathcal{M} \cap D(A),$$

where $D(A)$ denotes the domain of A , which is dense in \mathcal{H} . In this section we assume that the nonseparable remainder B is bounded:

$$(4.3) \quad \|B\varphi\| \leq \beta \|\varphi\|$$

for all $\varphi \in \mathcal{H}$. We need that every point $u \in \mathcal{M}$ is an element of its tangent space,

$$(4.4) \quad u \in T_u\mathcal{M} \quad \text{for all } u \in \mathcal{M},$$

which is satisfied if real multiples of elements of \mathcal{M} are again in \mathcal{M} . The curvature of \mathcal{M} is bounded in terms of the orthogonal projectors $P(u) : \mathcal{H} \rightarrow T_u\mathcal{M}$ and $Q(u) = I - P(u)$:

$$(4.5) \quad \|(P(u) - P(v))\varphi\| \leq \kappa \|u - v\| \cdot \|\varphi\|,$$

$$(4.6) \quad \|Q(v)(u - v)\| \leq \kappa \|u - v\|^2$$

for all $u, v \in \mathcal{M}$ and $\varphi \in \mathcal{H}$. The projection P is assumed continuously differentiable in the sense that $P(u(t))\varphi$ is a continuously differentiable function of t in \mathcal{H} for any continuously differentiable path $u(t)$ on \mathcal{M} and $\varphi \in \mathcal{H}$.

We assume that the initial value $\psi(0)$ is on \mathcal{M} and of unit norm. We consider a time interval on which the exact solution $\psi(t)$ remains near \mathcal{M} , in the sense that

$$(4.7) \quad \operatorname{dist}(\psi(t), \mathcal{M}) \leq \frac{1}{2\kappa} \quad \text{for } 0 \leq t \leq \bar{t}.$$

Both the exact solution $\psi(t)$ and the variational approximation $u(t)$ of (2.2) are required to be in the domain of H for $0 \leq t \leq \bar{t}$, with

$$(4.8) \quad \|H\psi(t)\| \leq \mu, \quad \|Hu(t)\| \leq \mu.$$

Further, we consider the distance bound $\delta \leq \mu$ given by

$$(4.9) \quad \operatorname{dist}(iH\psi(t), T_{v(t)}\mathcal{M}) \leq \delta, \quad \operatorname{dist}(iHu(t), T_{u(t)}\mathcal{M}) \leq \delta,$$

with $v(t) \in \mathcal{M}$ the nearest point to $\psi(t)$ on \mathcal{M} , i.e., $\|v(t) - \psi(t)\| = \operatorname{dist}(\psi(t), \mathcal{M})$.

4.2. Discussion of the assumptions. The critical assumption is the boundedness of the nonseparable remainder B . This condition is not satisfied in the adiabatic approximation, where $B = T_N$ is the kinetic energy operator of the nuclei, nor in the Hartree-Fock approximation of the electronic Schrödinger equation where the Coulomb potentials are nonseparable and unbounded. The boundedness of B is, however, a reasonable assumption in the Schrödinger equation (3.5) of the nuclei and its Hartree and Gaussian wave packet approximations (and their multiconfiguration versions). In the Hartree method, the best choice of A is $A = T_N + V_1 + \cdots + V_n$, where the single-particle potentials $V_k = V_k(x_k)$ are chosen to minimize the norm of the coupling potential $B = H - A$.

For simplicity we have assumed the splitting (4.1) to be independent of time. The results would, however, directly extend to the situation of a time-dependent splitting $H = A(t) + B(t)$, choosing for example $A(t) = T_N + V_1 + \cdots + V_n$ with V_k of (3.9) for the Hartree method. This might give more favourable error bounds than a time-independent splitting.

Conditions (4.2) and (4.4) are satisfied for all the examples in Section 3. Conditions (4.5) and (4.6) encode the curvature of \mathcal{M} in a form that is suitable for the analysis. Condition (4.7) ensures that $\psi(t)$ has a unique nearest point on \mathcal{M} . The regularity assumption (4.8) for $\psi(t)$ is satisfied if the initial value has such regularity. The regularity (4.8) of the approximate solution $u(t)$ is less easy to guarantee *a priori*. It can indeed be proved for the (multiconfiguration) time-dependent Hartree method when the Schrödinger equation for the nuclei has a smooth bounded potential [10]. In the Gaussian wave packet approximation, condition (4.8) with a moderate bound μ excludes extremely localized wave packets.

4.3. Near-optimality. The Dirac-Frenkel-McLachlan variational principle yields approximations whose error over sufficiently short time intervals is of the same magnitude as the distance from the exact wave function to the approximation manifold:

Theorem 4.1. *Under the conditions of Section 4.1, the error of the variational approximation is bounded by*

$$(4.10) \quad \|u(t) - \psi(t)\| \leq d(t) + Ce^{Kt} \int_0^t d(s) ds \quad \text{with} \quad d(t) = \text{dist}(\psi(t), \mathcal{M})$$

and with $K = 2\kappa\delta$ and $C = \beta + \kappa(\beta + 3\mu)$, for $0 \leq t \leq \bar{t}$.

Though the bound (4.10) may be pessimistic in a concrete situation, it clearly indicates the sources that can make the variational approximation deviate far from optimality even if the modeling error $d(t)$ is small: large curvature of the approximation manifold (κ), a large effective nonseparable potential in the Hamiltonian (β, δ), lack of regularity in the exact or approximate solution (μ, δ), and long time intervals (t).

4.4. Proof. The proof compares the differential equation for $u(t)$ with the equation satisfied by the best approximation $v(t) \in \mathcal{M}$ with $\|v(t) - \psi(t)\| = d(t)$.

(a) The function $v(t)$ is implicitly characterized by the condition (omitting the obvious argument t in the sequel)

$$(4.11) \quad P(v)(v - \psi) = 0.$$

Under condition (4.7), the implicit function theorem can be used to show that this equation has a unique solution in the ball of radius $1/(2\kappa)$ around ψ , which

depends continuously differentiably on t . We derive a differential equation for $v(t)$ by differentiating (4.11) with respect to t ($\dot{} = d/dt$):

$$(4.12) \quad 0 = P(v)(\dot{v} - \dot{\psi}) + (P'(v) \cdot (v - \psi))\dot{v}$$

with $(P'(v) \cdot \varphi)\dot{v} = (d/dt)P(v(t))\varphi$ for $\varphi \in \mathcal{H}$. Since $\dot{v} \in T_v\mathcal{M}$, we have $P(v)\dot{v} = \dot{v}$, and the equation becomes

$$(4.13) \quad \left(I + P'(v) \cdot (v - \psi)\right)\dot{v} = P(v)\dot{\psi}.$$

By (4.5) and (4.7) we have

$$\|P'(v) \cdot (v - \psi)\| \leq \kappa \|v - \psi\| \leq \frac{1}{2},$$

so that the operator in (4.13) is invertible and

$$(4.14) \quad \dot{v} = P(v)\dot{\psi} + r(v, \psi) \quad \text{with} \quad \|r(v, \psi)\| \leq 2\kappa\mu \|v - \psi\|.$$

Here we have used the bound (4.8), $\|\dot{\psi}\| = \|H\psi\| \leq \mu$. Inserting (2.1) in (4.14), the equation can be written as

$$(4.15) \quad \dot{v} = P(v)\frac{1}{i}Hv - P(v)\frac{1}{i}H(v - \psi) + r(v, \psi).$$

We will compare this differential equation with the equation (2.3) for $u(t)$. In the following we tacitly assume $v(t) \in D(H) = D(A)$. If v does not have this regularity, then the proof would proceed by replacing v by a regularized family (v_ϵ) with $v_\epsilon(t) \in D(H)$ and $v_\epsilon \rightarrow v$ in $C^1([0, \bar{t}], \mathcal{H})$ as $\epsilon \rightarrow 0$. Applying the arguments below to v_ϵ and letting $\epsilon \rightarrow 0$ in the final estimate then gives the result.

(b) We form the difference of (2.3) and (4.15), take the inner product with $u - v$ and take the real part. We then have

$$\|u - v\| \cdot \frac{d}{dt} \|u - v\| = \frac{1}{2} \frac{d}{dt} \|u - v\|^2 = \operatorname{Re} \langle u - v, \dot{u} - \dot{v} \rangle = I + II + III$$

with

$$\begin{aligned} I &= -\operatorname{Re} \langle u - v, P(u)iHu - P(v)iHv \rangle, \\ II &= -\operatorname{Re} \langle u - v, P(v)iH(v - \psi) \rangle, \\ III &= -\operatorname{Re} \langle u - v, r(v, \psi) \rangle. \end{aligned}$$

(c) Using the self-adjointness of $H = A + B$ and condition (4.2), which implies $Q(v)iAv = 0$, we write

$$\begin{aligned} I &= \operatorname{Re} \langle u - v, Q(u)iHu - Q(v)iHv \rangle \\ &= \operatorname{Re} \langle u - v, Q(u)iHu \rangle - \operatorname{Re} \langle u - v, Q(v)iBv \rangle. \end{aligned}$$

To treat the expression II , we split

$$II = -\operatorname{Re} \langle u - v, P(v)iA(v - \psi) \rangle - \operatorname{Re} \langle u - v, P(v)iB(v - \psi) \rangle.$$

It is in the first term that the condition (4.4) comes into play. This condition implies $P(v)v = v$ and hence, by (4.11),

$$v = P(v)\psi, \quad v - \psi = Q(v)(v - \psi) = -Q(v)\psi.$$

It follows that

$$\langle v, P(v)iA(v - \psi) \rangle = -\langle v, P(v)iAQ(v)\psi \rangle = \langle Q(v)iAv, \psi \rangle = 0,$$

since $Q(v)iAv = 0$ by (4.2). Similarly, (4.2) implies

$$\langle u, iAQ(u)(v - \psi) \rangle = 0.$$

These equations yield

$$\begin{aligned}
& \langle u - v, P(v) iA(v - \psi) \rangle \\
&= \langle u, iA(v - \psi) \rangle - \langle u - v, Q(v) iA(v - \psi) \rangle \\
&= -\langle u, iA(Q(u) - Q(v))(v - \psi) \rangle + \langle u - v, Q(v) iA\psi \rangle \\
&= -\langle iAu, (P(u) - P(v))(v - \psi) \rangle + \langle Q(v)(u - v), Q(v) iH\psi \rangle \\
&\quad - \langle u - v, Q(v) iB\psi \rangle .
\end{aligned}$$

This gives the basic identity of the proof,

$$\begin{aligned}
I + II &= \operatorname{Re} \langle Q(u)(u - v), Q(u) iHu \rangle - \operatorname{Re} \langle u - v, iB(v - \psi) \rangle \\
&\quad + \operatorname{Re} \langle iAu, (P(u) - P(v))(v - \psi) \rangle - \operatorname{Re} \langle Q(v)(u - v), Q(v) iH\psi \rangle .
\end{aligned}$$

With (4.3)–(4.9) we thus obtain

$$\begin{aligned}
|I + II| &\leq \kappa \|u - v\|^2 \cdot \delta + \|u - v\| \cdot \beta \|v - \psi\| \\
&\quad + (\mu + \beta) \cdot \kappa \|u - v\| \cdot \|v - \psi\| + \kappa \|u - v\|^2 \cdot \delta \\
&= 2\kappa\delta \|u - v\|^2 + (\beta + \kappa(\mu + \beta)) \|u - v\| \cdot \|v - \psi\| .
\end{aligned}$$

(d) Together with the bound (4.14) this estimate gives

$$\frac{d}{dt} \|u - v\| \leq K \|u - v\| + C \|v - \psi\|$$

with $K = 2\kappa\delta$ and $C = \beta + \kappa(\beta + 3\mu)$. The Gronwall inequality then implies

$$(4.16) \quad \|u(t) - v(t)\| \leq Ce^{Kt} \int_0^t \|v(s) - \psi(s)\| ds ,$$

and the triangle inequality for $u - \psi = (u - v) + (v - \psi)$ together with $d = \|v - \psi\|$ yields the result.

4.5. Time-dependent approximation manifolds. Theorem 4.1 extends readily to the case of time-dependent approximation manifolds \mathcal{M}_t that vary smoothly with t : we then have time-dependent projections $P(t, u) : \mathcal{H} \rightarrow T_u(\mathcal{M}_t)$, for which we assume the bound

$$\left\| \frac{\partial P}{\partial t}(t, u) \varphi \right\| \leq \rho \|\varphi\|$$

for all $\varphi \in \mathcal{H}$ and $u \in \mathcal{M}$. For $Q(t, u) = I - P(t, u)$ and $s(t, u)$ of (2.7) we assume

$$\|Q(t, u)s(t, u)\| \leq \sigma$$

for $u \in \mathcal{M}_t$ and $0 \leq t \leq \bar{t}$. Suppose all the bounds of Section 4.1 hold uniformly in t , and replace the bound δ of (4.9) by the corresponding bound for time-dependent manifolds \mathcal{M}_t ,

$$\operatorname{dist}(iH\psi(t) + s(t, v(t)), T_{v(t)}\mathcal{M}_t) \leq \delta , \quad \operatorname{dist}(iHu(t) + s(t, u(t)), T_{u(t)}\mathcal{M}_t) \leq \delta .$$

Then the error bound (4.10) remains valid with $d(t) = \operatorname{dist}(\psi(t), \mathcal{M}_t)$ and with constants

$$(4.17) \quad K = 2\kappa\delta , \quad C = \beta + 2\rho + \kappa(\beta + 3\mu + 2\sigma) .$$

The only major change in the proof is in part (a), where $v(t)$ now satisfies the differential equation

$$\dot{v} = P(t, v)\dot{\psi} + Q(t, v)s(t, v) + r(t, v, \psi)$$

with $\|r(t, v, \psi)\| \leq 2(\kappa(\mu + \sigma) + \rho) \|v - \psi\|$,

which is to be compared with

$$\dot{u} = P(t, u)\frac{1}{i}Hu + Q(t, u)s(t, u).$$

By the same arguments as in the proof of Theorem 4.1 we then obtain the error bound (4.10) with (4.17). Note that $\kappa = 0$ for linear spaces \mathcal{M}_t , as in Section 3.4.

5. AN ERROR BOUND FOR THE CASE OF COULOMB POTENTIALS

In this section we give an error bound in terms of approximation distances of the exact wave function which applies in situations where the coupling potential is unbounded. The distance of ψ to \mathcal{M} must now be taken with respect to a stronger norm, and in addition the distance from the time derivative $d\psi/dt$ to a tangent space of \mathcal{M} enters the estimate. The error bound applies to the time-dependent Hartree-Fock approximation of the electronic Schrödinger equation.

5.1. Assumptions. We assume again all conditions of Section 4.1, with the exception of the bound (4.3) for B . Now let A be positive definite. Then A defines an inner product on \mathcal{H}^1 , the domain of $A^{1/2}$,

$$(\chi, \varphi) \in \mathcal{H}^1 \times \mathcal{H}^1 \mapsto \langle \chi | A | \varphi \rangle, \quad \text{with the norm} \quad \|\varphi\|_1 = \langle \varphi | A | \varphi \rangle^{1/2},$$

by extension of $\langle \chi | A | \varphi \rangle = \langle \chi, A\varphi \rangle$ for $\chi \in \mathcal{H}^1$ and φ in the domain of A . We may assume $\|\varphi\| \leq \|\varphi\|_1$ for all $\varphi \in \mathcal{H}^1$. Instead of the bound (4.3) we take the weaker condition

$$(5.1) \quad \|B\varphi\| \leq \beta_1 \|\varphi\|_1$$

for all $\varphi \in \mathcal{H}^1$. For the manifold \mathcal{M} we now assume that the tangent space $T_v\mathcal{M}$ for $v \in \mathcal{M}$ is complex linear. We introduce the A -orthogonal projection $P_1(v) : \mathcal{H}^1 \rightarrow T_v\mathcal{M}$ as

$$P_1(v)\varphi = \vartheta \in T_v\mathcal{M} \quad \text{with} \quad \|\vartheta - \varphi\|_1 = \min !$$

This projection is characterized by $\langle \delta v | A | P_1(v)\varphi \rangle = \langle \delta v | A | \varphi \rangle$ for all $\delta v \in T_v\mathcal{M} \cap \mathcal{H}^1$, $\varphi \in \mathcal{H}^1$. We denote by $Q_1(v) = I - P_1(v)$ the complementary projection. $P_1(v)$ is not, in general, a bounded operator on \mathcal{H} , but for v in the domain of A the following condition turns out to make sense:

$$(5.2) \quad \langle \chi, P_1(v)\varphi \rangle \leq \rho_1 \|Av\| \cdot \|\chi\| \cdot \|\varphi\|$$

for all $\varphi, \chi \in \mathcal{H}^1$ (and then, via continuation by density, for all $\varphi, \chi \in \mathcal{H}$). We need the analogues of conditions (4.5)–(4.6) for the \mathcal{H}^1 -projections,

$$(5.3) \quad \|(P_1(u) - P_1(v))\varphi\|_1 \leq \kappa_1 \|u - v\|_1 \cdot \|\varphi\|_1,$$

$$(5.4) \quad \|Q_1(v)(u - v)\|_1 \leq \kappa_1 \|u - v\|_1^2,$$

and for the distance dist_1 with respect to the \mathcal{H}^1 -norm of the exact solution to the approximation manifold, the analogue of (4.7):

$$(5.5) \quad \text{dist}_1(\psi(t), \mathcal{M}) \leq \frac{1}{2\kappa_1} \quad \text{for} \quad 0 \leq t \leq \bar{t}.$$

We make the following regularity assumptions: the time derivative of the solution is bounded in the \mathcal{H}^1 -norm,

$$(5.6) \quad \left\| \frac{d\psi}{dt}(t) \right\|_1 \leq \mu_1 \quad \text{for } 0 \leq t \leq \bar{t},$$

and the \mathcal{H}^1 -nearest point to $\psi(t)$ on \mathcal{M} , i.e., $v_1(t) \in \mathcal{M}$ with $\|v_1(t) - \psi(t)\|_1 = \text{dist}_1(\psi(t), \mathcal{M})$, is in the domain of A and satisfies

$$(5.7) \quad \|Av_1(t)\| \leq \nu_1 \quad \text{for } 0 \leq t \leq \bar{t}.$$

We denote by $\delta_1 \leq \mu$ (see (4.8)) the bound

$$(5.8) \quad \text{dist}(iH\psi(t), T_{v_1(t)}\mathcal{M}) \leq \delta_1, \quad \text{dist}(iHu(t), T_{u(t)}\mathcal{M}) \leq \delta_1.$$

5.2. Verification of the assumptions for Hartree and Hartree-Fock approximations. The assumptions are satisfied for the time-dependent Hartree-Fock approximation of the electronic Schrödinger equation (3.3). Here $A = T_e + I$ is the (shifted) kinetic energy operator and $B = U(x, \cdot) - I$ the Coulomb potential for fixed coordinates x of the nuclei. The Hilbert space is $\mathcal{H} = L^2(\mathbf{R}^{3\ell})$, and \mathcal{H}^1 is the Sobolev space $H^1(\mathbf{R}^{3\ell})$.

The bound (5.1) is a consequence of Hardy's inequality ([9, p. 350, (4.24)], [16, (3.7)]). In the following we give the proof of (5.2) and (5.7) for the Hartree method (3.8) with products of only two functions (without antisymmetrization). The same arguments apply to Hartree products with any number of factors and to the antisymmetrized functions in the Hartree-Fock method (3.11), but the presentation becomes more cumbersome.

Proof of (5.2). Let $v = \phi_1 \otimes \phi_2 \in \mathcal{M} \cap H^2$ and assume for simplicity $\|\phi_1\| = \|\phi_2\| = 1$. The operator A takes the form $A = A_1 \otimes I + I \otimes A_2$, where A_j is a shifted and scaled negative Laplacian acting on functions of the variable x_j ($j = 1, 2$). For $\varphi \in H^2$, consider the projection $\vartheta = P_1(v)\varphi \in T_v\mathcal{M}$, which can be uniquely written as

$$\vartheta = \theta_1 \otimes \phi_2 + \phi_1 \otimes \theta_2 + c \phi_1 \otimes \phi_2$$

with $\langle \theta_j | A_j | \phi_j \rangle = 0$ for $j = 1, 2$ and a complex number c . We then have

$$\|\theta_1\|_1^2 = \langle \theta_1 | A_1 | \theta_1 \rangle = \langle \theta_1 \otimes \phi_2 | A_1 \otimes I | \theta_1 \otimes \phi_2 \rangle = \langle \theta_1 \otimes \phi_2 | A_1 \otimes I | \vartheta \rangle$$

and similarly for θ_2 . Hence,

$$(5.9) \quad \|\theta_1\|_1 \leq \|\vartheta\|_1, \quad \|\theta_2\|_1 \leq \|\vartheta\|_1, \quad |c| \leq \|\vartheta\| + \|\theta_1\| + \|\theta_2\| \leq 3\|\vartheta\|_1.$$

Since ϑ is determined by the condition

$$(5.10) \quad \langle \delta_1 \otimes \phi_2 + \phi_1 \otimes \delta_2 | A | \vartheta \rangle = \langle \delta_1 \otimes \phi_2 + \phi_1 \otimes \delta_2 | A | \varphi \rangle$$

for arbitrary $\delta_1 \in H_{x_1}^1$, $\delta_2 \in H_{x_2}^1$, we obtain the equation

$$A_1\theta_1 + A_1\phi_1 \langle \phi_2, \theta_2 \rangle + cA_1\phi_1 + \theta_1 \langle \phi_2, A_2\phi_2 \rangle + c\phi_1 \langle \phi_2, A_2\phi_2 \rangle = \langle \phi_2, A\varphi \rangle_{x_2}$$

and the same equation with the subscripts 1 and 2 interchanged. From this we see that the L^2 norm of $A_1\theta_1$ can be bounded in terms of the L^2 norms of $A_j\phi_j$ ($j = 1, 2$) and $A\varphi$, with the bound

$$\|A_1\theta_1\| \leq \|A_1\phi_1\| \cdot \|\theta_2\| + \|A_2\phi_2\| \cdot \|\theta_1\| + |c| \cdot (\|A_1\phi_1\| + \|A_2\phi_2\|) + \|A\varphi\|$$

and the same bound for $\|A_2\theta_2\|$. We now note that

$$\|A_1\phi_1\|^2 + \|A_2\phi_2\|^2 = \|(A_1 \otimes I)v\|^2 + \|(I \otimes A_2)v\|^2 \leq \|Av\|^2$$

where the last inequality is obtained using the Plancherel identity and estimating the Fourier transforms. With $\|\theta_j\| \leq \|\theta_j\|_1$, the bounds (5.9), and $\|\vartheta\|_1 \leq \|\varphi\|_1 \leq \|A\varphi\|$, these inequalities give (with $\rho_1 = 16$)

$$(5.11) \quad \|AP_1(v)\varphi\| \leq \rho_1 \|Av\| \cdot \|A\varphi\|.$$

We write

$$\langle \chi, P_1(v)\varphi \rangle = \langle A^{-1}\chi | A | P_1(v)\varphi \rangle = \langle P_1(v)A^{-1}\chi | A | \varphi \rangle = \langle AP_1(v)A^{-1}\chi, \varphi \rangle,$$

and since $\|AP_1(v)A^{-1}\chi\| \leq \rho_1 \|Av\| \cdot \|\chi\|$ by (5.11), we obtain (5.2).

Proof of (5.7). We note that v_1 satisfies $P_1(v_1)(v_1 - \psi) = 0$ and hence, by (4.4),

$$v_1 = P_1(v_1)\psi.$$

In particular, $\|v_1\|_1 \leq \|\psi\|_1$. In view of (5.10) with $\vartheta = v_1 = \phi_1 \otimes \phi_2$ and $\varphi = \psi$, we have

$$A_1\phi_1\|\phi_2\|^2 + \phi_1\|\phi_2\|_1^2 = \langle \phi_2, A\psi \rangle_{x_2}$$

and the same equation with the subscripts 1 and 2 interchanged. With the bound (4.8) for $A\psi$, this yields (5.7) as long as $\|v_1\| \geq \frac{1}{2}$, say. Since $\|v_1 - \psi\| \leq \|v_1 - \psi\|_1 = \text{dist}_1(\psi, \mathcal{M})$ and $\|\psi\| = 1$, the latter condition is satisfied if $\text{dist}_1(\psi, \mathcal{M}) \leq \frac{1}{2}$.

5.3. Error bound.

Theorem 5.1. *Under the conditions of Section 4.1 (with the exception of (4.3)) and of Section 5.1, the error of the variational approximation is bounded by*

$$(5.12) \quad \|u(t) - \psi(t)\| \leq d_1(t) + e^{K_1 t} \int_0^t \left(C_1 d_1(s) + C^* d^*(s) \right) ds$$

with $d_1(t) = \text{dist}_1(\psi(t), \mathcal{M})$, $d^*(t) = \text{dist}(\frac{d\psi}{dt}(t), T_{v_1(t)}\mathcal{M})$ and with the constants $K_1 = 2\kappa\delta_1$, $C_1 = \beta_1 + 2\kappa_1\mu_1$, $C^* = \rho_1\nu_1$, for $0 \leq t \leq \bar{t}$.

5.4. Proof. By the same argument as in part (a) of the proof of Theorem 4.1, the function $v_1(t)$ satisfies

$$(5.13) \quad P_1(v_1)(v_1 - \psi) = 0$$

and the differential equation

$$(5.14) \quad \dot{v}_1 = P_1(v_1)\dot{\psi} + r_1(v_1, \psi) \quad \text{with} \quad \|r_1(v_1, \psi)\|_1 \leq 2\kappa_1\mu_1 \|v_1 - \psi\|_1.$$

We rewrite this as

$$(5.15) \quad \dot{v}_1 = -P(v_1)iHv_1 - P(v_1)iH(\psi - v_1) - (P_1(v_1) - P(v_1))iH\psi + r_1(v_1, \psi).$$

We form the difference of (2.3) and (5.15), take the \mathcal{H} -inner product with $u - v_1$ and take the real part. We then have

$$\|u - v_1\| \cdot \frac{d}{dt} \|u - v_1\| = I + II + III + IV$$

with

$$\begin{aligned} I &= -\text{Re} \langle u - v_1, P(u)iHu - P(v_1)iHv_1 \rangle, \\ II &= -\text{Re} \langle u - v_1, P(v_1)iH(v_1 - \psi) \rangle, \\ III &= \text{Re} \langle u - v_1, (P_1(v_1) - P(v_1))iH\psi \rangle, \\ IV &= -\text{Re} \langle u - v_1, r_1(v_1, \psi) \rangle. \end{aligned}$$

As in part (c) of the proof of Theorem 4.1, we have

$$I = \operatorname{Re} \langle u - v_1, Q(u) i H u \rangle - \operatorname{Re} \langle u - v_1, Q(v_1) i H v_1 \rangle .$$

For the term II we note that, using (5.13),

$$\langle u - v_1, P(v_1) i A (v_1 - \psi) \rangle = i \langle P(v_1)(u - v_1) | A | Q_1(v_1)(v_1 - \psi) \rangle = 0 ,$$

because $P(v_1)(u - v_1) \in T_{v_1} \mathcal{M}$ and the range of $Q_1(v_1)$ is A -orthogonal to $T_{v_1} \mathcal{M}$. Hence,

$$\begin{aligned} I + II &= \operatorname{Re} \langle Q(u)(u - v_1), Q(u) i H u \rangle - \operatorname{Re} \langle Q(v_1)(u - v_1), Q(v_1) i H \psi \rangle \\ &\quad - \operatorname{Re} \langle u - v_1, i B (v_1 - \psi) \rangle , \end{aligned}$$

which by (5.1) is bounded by

$$|I + II| \leq 2\kappa \|u - v_1\|^2 \cdot \delta_1 + \|u - v_1\| \cdot \beta_1 \|v_1 - \psi\|_1 .$$

The expression III is rewritten as

$$III = \operatorname{Re} \langle u - v_1, P_1(v_1) Q(v_1) \dot{\psi} \rangle ,$$

and (5.2) and (5.7) yield

$$(5.16) \quad |III| \leq \rho_1 \nu_1 \|u - v_1\| \cdot \operatorname{dist}(\dot{\psi}, T_{v_1} \mathcal{M}) .$$

In total, we obtain

$$\frac{d}{dt} \|u - v_1\| \leq K_1 \|u - v_1\| + C_1 d_1 + C^* d^*$$

with the constants K_1 , C_1 , C^* given in the theorem. The Gronwall inequality and the triangle inequality together with $\|v_1 - \psi\| \leq \|v_1 - \psi\|_1 = d_1$ then yield the result.

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MATHEMATISCHES INSTITUT, UNIVERSITÄT TÜBINGEN, AUF DER MORGENSTELLE 10, D-72076 TÜBINGEN, GERMANY

E-mail address: `lubich@na.uni-tuebingen.de`

URL: `http://na.uni-tuebingen.de`