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Jürg Hutter, Michele Parrinello, and Stefan Vogel

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Exponential transformation of molecular orbitals

Jürg Hutter and Michele Parrinello

IBM Research Division, Zurich Research Laboratory, 8803 Rüschlikon, Switzerland

Stefan Vogel

Rechenzentrum der Universität Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland

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In this paper we present new formulas related to the parametrization of molecular orbitals by exponential transformations. We show that it is not necessary to use series expansions of the exponentials and that the first derivative of the energy with respect to independent parameters can be calculated at arbitrary positions in an efficient manner. These formulas can be implemented such that computational costs are of order N^2M and storage requirements of order NM , where N is the number of occupied orbitals and M the size of the basis set. We discuss possible applications to Hartree–Fock calculations and *ab initio* molecular dynamics.

I. INTRODUCTION

Current approaches to the solution of Hartree–Fock equations and to density functional theory are based on nonlinear optimization methods. Requiring orthogonality of the single-particle orbitals imposes constraints if the orbitals are parametrized by expansion coefficients in some basis set. These constraints can be taken into account by the method of Lagrange multipliers as proposed by Roothaan¹ and Hall² for Hartree–Fock and Kohn and Sham³ for density functional theory. The resulting Roothaan–Hall or Kohn–Sham equations are traditionally solved by a fixed-point iterative procedure involving matrix diagonalization. A similar approach is taken by Car–Parrinello molecular dynamics,⁴ which avoids diagonalization but requires the solution of a system of coupled nonlinear equations to calculate the Lagrange multipliers. Powerful extrapolation schemes were developed to accelerate convergence of the iterative procedure.⁵

No constraints are necessary if the orbitals are described by a unitary transformation of some set of orthogonal reference orbitals^{6–9} because the resulting orbitals are orthogonal by construction. One possible set of parameters is the set of Givens rotation angles, which was investigated by Head-Gordon and Pople.¹⁰ They found that the number of operations scales as $O(N^2M^2)$ and the storage requirements as $O(M^2)$ where N is the number of occupied orbitals and M the size of the basis set. The operation count can be reduced by resetting the rotation angles to zero after each optimization step. However, such a change of variables would make this approach incompatible with quasi-Newton optimization methods or the requirements of Car–Parrinello molecular dynamics. Another parametrization of the unitary transformation is obtained by considering the fact that any unitary matrix can be written as the exponential of a skew-Hermitian matrix. Head-Gordon and Pople¹⁰ report the same scaling behavior as for the case of Givens rotations if exponentials are evaluated using series expansion. These findings effectively hamper the use of the above ideas for many applications. Therefore the concept of orbital rotations is most popular for multiconfigurational Hartree–Fock calculations,^{11,12} where the operation count of the computationally dominant

part scales as $O(M^4)$ or worse. In contrast, current approaches to Hartree–Fock and density functional theory based on direct methods¹³ scale better than $O(M^3)$ in the operation count and as $O(NM)$ in storage. A further obstacle to the application of exponentiation-based parametrizations to problems requiring large basis sets is the lack of an explicit, efficiently computable expression for the derivative of the unitary transformation with respect to elements of the skew-Hermitian matrix.

In this note we will demonstrate a method to evaluate exponentials as well as their derivatives efficiently with the same scaling behavior of computational costs and storage requirements as local density functional methods using plane wave basis sets.

II. ORBITAL ROTATIONS

A set of N molecular orbitals (MO) Φ_i can be expanded in a finite basis set ψ_j of dimension M as

$$\Phi_i = \sum_{j=1}^M c_{ji} \psi_j, \quad i = 1, \dots, N. \quad (1)$$

We represent formally the set of MO as an $M \times N$ matrix $C_0 = \{c_{ji}\}$. Orthogonality of the MO requires that

$$C_0^\dagger C_0 = I_N, \quad (2)$$

where S is the overlap matrix of the basis functions and I_N is the unit matrix in N dimensions. We then write

$$C = C_i \exp(A), \quad (3)$$

where C_i and A are $M \times M$ matrices, $C_i^\dagger S C_i = I_M$ and $A^\dagger = -A$. The notation C also represents an $M \times M$ matrix; the submatrix of its first N columns coincides with C_0 and is the only relevant part. By construction C is a unitary matrix.

The total energy $E(\mathbf{C}_0)$ is invariant with respect to rotations within the column vectors of \mathbf{C}_0 :

$$E(\mathbf{C}_0) = E(\mathbf{C}_0 \mathbf{U}), \quad (4)$$

where \mathbf{U} is an $N \times N$ unitary matrix. Using this and the fact that the energy does not depend on the last $(M-N)$ columns of \mathbf{C} we parametrize \mathbf{A} in the form

$$\mathbf{A} = \begin{pmatrix} 0 & \mathbf{X} \\ -\mathbf{X}^\dagger & 0 \end{pmatrix}, \quad (5)$$

where \mathbf{X} is an $N \times (M-N)$ matrix. For this special form of \mathbf{A} , $\exp(\mathbf{A})$ can be explicitly written in terms of block matrices as:

$$\exp(\mathbf{A}) = \begin{pmatrix} \cos \mathbf{P}^{1/2} & \mathbf{P}^{-1/2} \sin \mathbf{P}^{1/2} \mathbf{X} \\ -\mathbf{X}^\dagger \mathbf{P}^{-1/2} \sin \mathbf{P}^{1/2} & \mathbf{I}_{M-N} + \mathbf{X}^\dagger (\cos \mathbf{P}^{1/2} - \mathbf{I}_N) \mathbf{P}^{-1} \mathbf{X} \end{pmatrix}, \quad (6)$$

where $\mathbf{P} = \mathbf{X} \mathbf{X}^\dagger$ is an $N \times N$ matrix. Equation (6) can be derived by using the assumed form of \mathbf{A} in the series expansion

$$\exp(\mathbf{A}) = 1 + \frac{\mathbf{A}}{1!} + \frac{\mathbf{A}^2}{2!} + \dots \quad (7)$$

and resumming the terms. The expression for \mathbf{C}_0 then becomes

$$\mathbf{C}_0 = \mathbf{C}_1 \begin{pmatrix} \cos \mathbf{P}^{1/2} \\ -\mathbf{X}^\dagger \mathbf{P}^{1/2} \sin \mathbf{P}^{1/2} \end{pmatrix}. \quad (8)$$

This allows the energy to be calculated explicitly as a function of \mathbf{X} . It is of great practical importance that it is possible to calculate \mathbf{X} from a given \mathbf{C}_0 and any arbitrary choice of \mathbf{C}_1 . This can be done using the invariance of the energy E with respect to unitary rotations of \mathbf{C}_0 . We first define two new matrices $\tilde{\mathbf{C}}_1$ and $\tilde{\mathbf{C}}_2$ of dimension $N \times N$ and $(M-N) \times N$:

$$\mathbf{C}_1^\dagger \mathbf{C}_0 = \begin{pmatrix} \tilde{\mathbf{C}}_1 \\ \tilde{\mathbf{C}}_2 \end{pmatrix}. \quad (9)$$

If we now find a unitary $N \times N$ matrix \mathbf{U} that rotates $\tilde{\mathbf{C}}_1$ into a Hermitian matrix \mathbf{C}_1 , then we can solve

$$\mathbf{C}_1 = \cos \mathbf{P}^{1/2}, \quad (10)$$

for \mathbf{P} by diagonalization of \mathbf{C}_1 , and calculate \mathbf{X} from

$$\mathbf{X} = -\mathbf{P}^{-1/2} (\sin \mathbf{P}^{1/2})^{-1} \mathbf{C}_2^\dagger, \quad (11)$$

where $\mathbf{C}_2 = \tilde{\mathbf{C}}_2 \mathbf{U}$. The matrix \mathbf{U} can be calculated by means of a singular value decomposition.¹⁴ The singular value decomposition of $\tilde{\mathbf{C}}_1$ can be written

$$\tilde{\mathbf{C}}_1 = \mathbf{V} \mathbf{\Sigma} \mathbf{W}^\dagger, \quad (12)$$

where \mathbf{V} and \mathbf{W} are unitary matrices and $\mathbf{\Sigma}$ is the diagonal matrix of the singular values. It is easy to see that the desired transformation can be achieved by a combination of the two matrices \mathbf{V} and \mathbf{W}

$$\mathbf{C}_1 = \tilde{\mathbf{C}}_1 \mathbf{U} = \tilde{\mathbf{C}}_1 \mathbf{W} \mathbf{V}^\dagger = \mathbf{V} \mathbf{\Sigma} \mathbf{V}^\dagger. \quad (13)$$

This shows that there is no loss of generality in parametrizing \mathbf{A} as done in Eq. (5).

III. GRADIENT

The calculation of the energy gradient can be performed using the chain rule

$$\frac{\partial E(\mathbf{C}_0(\mathbf{X}))}{\partial \mathbf{X}} = \frac{\partial E(\mathbf{C}_0(\mathbf{X}))}{\partial \mathbf{C}_0} \frac{\partial \mathbf{C}_0}{\partial \mathbf{X}}, \quad (14)$$

where the sum over all the relevant elements of matrices \mathbf{C}_0 and \mathbf{X} is understood. The term $\partial E(\mathbf{C}_0(\mathbf{X})) / \partial \mathbf{C}_0$ is obviously the usual unconstrained gradient. In order to calculate $\partial \mathbf{C}_0 / \partial \mathbf{X}$ the following operatorial formula is needed:

$$\frac{\partial \exp(\mathbf{A})}{\partial \mathbf{X}} = \int_0^1 dt \exp(\mathbf{A}t) \frac{\partial \mathbf{A}}{\partial \mathbf{X}} \exp(\mathbf{A}(1-t)). \quad (15)$$

This expression can be derived analogous to the Trotter formula

$$\begin{aligned} \frac{\partial \exp(\mathbf{A})}{\partial \mathbf{X}} &= \frac{\partial}{\partial \mathbf{X}} \left[\exp\left(\frac{\mathbf{A}}{p}\right) \right]^p \\ &= \sum_{i=1}^p \left[\exp\left(\frac{i-1}{p} \mathbf{A}\right) \frac{\partial \exp(\mathbf{A}/p)}{\partial \mathbf{X}} \exp\left(\frac{p-i}{p} \mathbf{A}\right) \right]. \end{aligned} \quad (16)$$

For large values of p one has

$$\frac{\partial}{\partial \mathbf{X}} \exp\left(\frac{\mathbf{A}}{p}\right) \approx \frac{1}{p} \frac{\partial \mathbf{A}}{\partial \mathbf{X}} \quad (17)$$

and setting $\Delta t = 1/p$ for $p \rightarrow \infty$, Eq. (15) is recovered. Specializing Eq. (15) to the case of a matrix \mathbf{A} with the structure given in Eq. (6) we obtain

$$\begin{aligned} \frac{\partial E(\mathbf{C}_0(\mathbf{X}))}{\partial \mathbf{X}} &= \mathbf{R}^\dagger \{ -[\mathbf{R}(\mathbf{G}^{(1)\dagger} + \mathbf{G}^{(1)})\mathbf{R}^\dagger] \otimes \mathbf{\Gamma}^{(1)} \\ &\quad - [\mathbf{R}(\mathbf{X}\mathbf{G}^{(2)} + \mathbf{G}^{(2)\dagger}\mathbf{X}^\dagger)\mathbf{R}^\dagger] \otimes \mathbf{\Gamma}^{(2)} \} \mathbf{R} \mathbf{X} \\ &\quad - \mathbf{R}^\dagger \mathbf{\Gamma}^{(3)} \mathbf{R} \mathbf{G}^{(2)\dagger}. \end{aligned} \quad (18)$$

Here, the symbol \otimes stands for multiplication by elements

$$\mathbf{Y}_{ij} = \{ \mathbf{U} \otimes \mathbf{V} \}_{ij} = \mathbf{U}_{ij} \mathbf{V}_{ij}. \quad (19)$$

The $N \times N$ matrices \mathbf{R} and $\mathbf{\Gamma}$ consist of the eigenvectors and eigenvalues of \mathbf{P} respectively

$$\mathbf{P} = \mathbf{R}^\dagger \mathbf{\Gamma} \mathbf{R}, \quad (20)$$

$$\Gamma_{ij} = \gamma_i^2 \delta_{ij}. \quad (21)$$

The unconstrained gradient $\partial E / \partial \mathbf{C}_0$ has been decomposed into a part $\mathbf{G}^{(1)}$, an $N \times N$ matrix, and $\mathbf{G}^{(2)}$, an $(M-N) \times N$ matrix

$$\frac{\partial E}{\partial \mathbf{C}_0} = \mathbf{C}_0^\dagger \mathbf{H} \mathbf{C}_0 = \begin{pmatrix} \mathbf{G}^{(1)} \\ \mathbf{G}^{(2)} \end{pmatrix}, \quad (22)$$

where \mathbf{H} is either the Hartree–Fock or the Kohn–Sham matrix expressed in the basis functions. The three matrices $\Gamma^{(1)}$, $\Gamma^{(2)}$, and $\Gamma^{(3)}$ are the results of the integration in Eq. (15). They can be expressed as functions of the square root of the eigenvalues of the \mathbf{P} matrix

$$\begin{aligned} \Gamma_{\alpha\beta}^{(1)} &= \frac{1}{2} j_0 \left(\frac{\gamma_\alpha + \gamma_\beta}{2} \right) j_0 \left(\frac{\gamma_\alpha - \gamma_\beta}{2} \right), \\ \Gamma_{\alpha\beta}^{(2)} &= \frac{j_0(\gamma_\alpha) - j_0(\gamma_\beta)}{\gamma_\alpha^2 - \gamma_\beta^2}, \\ \Gamma_{\alpha\beta}^{(3)} &= j_0(\gamma_\alpha) \delta_{\alpha\beta}, \end{aligned} \quad (23)$$

where j_0 is the spherical Bessel function of order zero.

IV. APPLICATIONS

In this section, we discuss possible applications of the formulas presented in this paper. The applications chosen are single-point Hartree–Fock (HF) calculations and *ab initio* molecular dynamics using density functional theory and plane-wave basis sets.

A. Hartree–Fock calculations

Since the advent of the direct approach to HF calculations with Gaussian basis sets, the issue of convergence acceleration has gained special attention. In their original paper Almlöf, Fægri, Jr., and Korsell¹³ advocate the use of orbital rotations in a Newton–Raphson scheme. The application of this second-order method and of the simpler quasi-Newton methods was restricted to small systems because of the storage requirements of the wave function Hessian. Recently, Fischer and Almlöf¹⁵ described a method that resolves the storage problem. For this they used Pulay's DIIS method⁵ in combination with a recursive update procedure¹⁶ for an approximate Hessian to reoptimize the wave function in geometry optimizations. Despite the fact that they set the rotation parameters to zero after each iteration, excellent convergence was achieved. Certainly only small rotations of the initial wave functions are needed in geometry optimizations and hence the inconsistency introduced in the Hessian is not of great importance. However, for the initial convergence of the wave function the use of a quasi-Newton method requires the consistent handling of the parameters as described in the present paper.

Parallel implementations of HF programs¹⁷ are so efficient that the sequential update of the wave functions becomes a bottleneck, especially if this involves a diagonalization of the Fock matrix of $O(M^3)$. The method presented in this paper allows a wave function update where only the matrix \mathbf{P} of dimension N has to be diagonalized sequentially. The other steps of the update of $O(N^2M)$ consist of matrix

multiplies that can be performed in parallel. A method with similar scaling properties has been presented recently by Shepard.¹⁸ The calculation of the wave functions from the orbital rotations and the calculation of the energy gradient only require the storage of intermediate quantities of size $O(NM)$. Therefore, the use of exponential transformations does not become prohibitive even for large basis set calculations, e.g., with uncontracted basis sets.

A generalization of the formalism to open-shell cases cannot be done in the usual way of redefining the matrix \mathbf{A}

$$\mathbf{A} = \begin{pmatrix} 0 & \mathbf{X}_{\text{co}} & \mathbf{X}_{\text{cv}} \\ -\mathbf{X}_{\text{co}}^\dagger & 0 & \mathbf{X}_{\text{ov}} \\ -\mathbf{X}_{\text{cv}}^\dagger & -\mathbf{X}_{\text{ov}}^\dagger & 0 \end{pmatrix}. \quad (24)$$

The subscripts **c**, **o**, and **v** denote closed-shell, open-shell, and virtual orbitals, respectively. This would destroy the special block structure of \mathbf{A} that constitutes the foundation of the formalism. However, we can keep the special structure by defining instead

$$\mathbf{C} = \mathbf{C}_1 \exp(\mathbf{A}_1) \exp(\mathbf{A}_2), \quad (25)$$

where the matrices \mathbf{A}_1 and \mathbf{A}_2 are defined by

$$\begin{aligned} \mathbf{A}_1 &= \begin{pmatrix} 0 & \tilde{\mathbf{X}}_{\text{co}} & \tilde{\mathbf{X}}_{\text{cv}} \\ -\tilde{\mathbf{X}}_{\text{co}}^\dagger & 0 & 0 \\ -\tilde{\mathbf{X}}_{\text{cv}}^\dagger & 0 & 0 \end{pmatrix}; \\ \mathbf{A}_2 &= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \tilde{\mathbf{X}}_{\text{ov}} \\ 0 & -\tilde{\mathbf{X}}_{\text{ov}}^\dagger & 0 \end{pmatrix}. \end{aligned} \quad (26)$$

This definition allows formulas for \mathbf{C}_0 and $\partial E / \partial \mathbf{X}$ to be derived along the same lines as for the closed-shell case. Generalization of this ansatz to more than one open shell is straightforward.

B. *Ab initio* molecular dynamics

In the Car–Parrinello method^{4,19,20} the equations of motion for the ionic and the fictitious electron dynamics are derived from the Lagrangian

$$\begin{aligned} \mathcal{L}_{\text{CP}} &= \mu \sum_i^N \int |\dot{\psi}_i(\mathbf{r})|^2 + \frac{1}{2} \sum_I M_I \dot{\mathbf{R}}_I^2 - E[\{\psi_i(\mathbf{r})\}, \{\mathbf{R}_I\}] \\ &\quad + \sum_{i,j}^N \Lambda_{ij} \left(\int d\mathbf{r} \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) - \delta_{ij} \right), \end{aligned} \quad (27)$$

where μ is the fictitious electron mass, M_I and \mathbf{R}_I the ionic mass and coordinates. We can define analogously a new Lagrangian where the orbital rotation parameters replace the orbitals as coordinates

$$\tilde{\mathcal{L}}_{\text{CP}} = \mu \sum_i^N \sum_j^M \dot{\mathbf{x}}_{ij}^2 + \frac{1}{2} \sum_I M_I \dot{\mathbf{R}}_I^2 - E[\{\psi_i(\mathbf{X})\}, \{\mathbf{R}_I\}]. \quad (28)$$

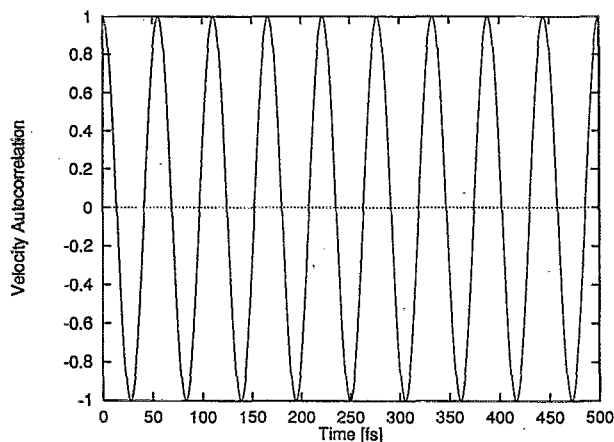


FIG. 1. Velocity autocorrelation function for the optical phonon in crystalline silicon.

As the orbitals are now orthogonal by construction, there is no constraint term in this Lagrangian. This Lagrangian generates dynamics for \mathbf{X} and \mathbf{R}_I through the equations of motion

$$\mu \ddot{\mathbf{X}}_{ij} = -\frac{1}{2} \frac{\delta E}{\delta \mathbf{X}_{ij}}, \quad (29)$$

$$M_I \ddot{\mathbf{R}}_I = -\frac{\partial E}{\partial \mathbf{R}_I}. \quad (30)$$

We implemented this molecular dynamics scheme in the standard Car–Parrinello code, where energies and forces are calculated within the pseudopotential and local density approximation to density functional theory, and plane waves are used as basis functions

$$\psi_n(\vec{r}) = \sum_{\vec{g}} c_{\vec{g}}^n e^{-i\vec{g}\vec{r}}. \quad (31)$$

Only the Γ point is used to sample the Brillouin zone. At the Γ point the wave functions are real and the expansion coefficients exhibit the following symmetry:

$$c_{\vec{g}}^i = (c_{-\vec{g}}^i)^*. \quad (32)$$

We have chosen the reference orbitals to be the most simple combination of plane waves that still shows this symmetry

$$\mathbf{C}_i = \frac{1}{\sqrt{2}} \begin{pmatrix} 1_K & 0 & i1_K \\ 0 & \sqrt{2} & 0 \\ 1_K & 0 & -i1_K \end{pmatrix}, \quad (33)$$

with $K = (M-1)/2$. To verify this new approach we performed a molecular dynamics run on the optical mode of crystalline silicon in the diamond structure. We used a simple cubic supercell of eight atoms with the experimental lattice parameter of 10.26 a.u., and the Hamann, Schlüter, and Chiang-type pseudopotential^{21,22} with s nonlocality in the Kleinman–Bylander scheme.²³ The plane-wave cutoff for the wave functions was 13 Ry, the time step was 10 a.u. and the mass μ was chosen to be 400 a.u. The trajectory was followed for 5 ps and the velocity autocorrelation function $C_{vv}(t)$ was calculated up to 500 fs

$$C_{vv}(t) = \frac{(1/N_I) \sum_I \langle \dot{\mathbf{R}}_I(0) \dot{\mathbf{R}}_I(t) \rangle}{(1/N_I) \sum_I \langle \dot{\mathbf{R}}_I(0) \dot{\mathbf{R}}_I(0) \rangle}, \quad (34)$$

where N_I is the number of atoms in the supercell. The velocity autocorrelation function in Fig. 1 shows that the system stays perfectly adiabatic for the 5 ps. A detailed investigation of all aspects of *ab initio* molecular dynamics with the use of orbital rotations will be made in a forthcoming paper.

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