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General and efficient algorithms for obtaining maximally localized Wannier functions

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Recent advances in the theory of polarization and the development of linear-scaling methods have revitalized interest in the use of Wannier functions for obtaining a localized orbital picture within a periodic supercell. To examine complex chemical systems it is imperative for the localization procedure to be efficient; on the other hand, the method should also be simple and general. Motivated to meet these requirements we derive in this paper a spread functional to be minimized as a starting point for obtaining maximally localized Wannier functions through a unitary transformation. The functional turns out to be equivalent to others discussed in the literature with the difference of being valid in simulation supercells of arbitrary symmetry in the Γ-point approximation. To minimize the spread an iterative scheme is developed and very efficient optimization methods, such as conjugate gradient, direct inversion in the iterative subspace, and preconditioning are applied to accelerate the convergence. The iterative scheme is quite general and is shown to work also for methods first developed for finite systems (e.g., Pipek-Mezey, Boys-Foster). The applications discussed range from crystal structures such as Si to isolated complex molecules and are compared to previous investigations on this subject.

I. INTRODUCTION

The representation of the electronic ground state in terms of localized Wannier orbitals[1] provides a powerful tool in the study of periodic solids. Recent advances in the formulation of a theory of electronic polarization[2,3] and the development of linear-scaling methods[4] have rejuvenated the use of Wannier functions as an analysis tool. Namely, Wannier functions afford an insightful picture to the nature of chemical bonding and aid in the understanding of classical chemical concepts (e.g., nonbonding electron pairs or valency) in terms of quantum mechanics.

In spite of this wide field of applications, a lack of a practical, general, and efficient methods to calculate Wannier functions is evident. This is in contrast to finite systems, where many different criteria for producing localized orbitals have been developed.[5–8]

Wannier functions (WF) are defined in terms of a unitary transformation performed on the occupied Bloch orbitals (BO).[1] One major problem in a practical calculation is their nonuniqueness. This is a result of the indeterminacy of the BO's, which are, in the case of a single band, only determined up to a phase factor, in the multiband case, up to an arbitrary unitary transformation among all occupied orbitals at every point in the Brillouin zone. As proposed recently by Marzari and Vanderbilt,[9] one can resolve this nonuniqueness by requiring that the total spread of the localized function is minimal. This criterion is in close analogy with the Boys-Foster method[5] for finite systems, here one uses the spread defined through the conventional position operator. The technique has been successfully applied to crystal systems and to small molecules within a general $\mathbf{k}$-point scheme.[9,10] An extension to disordered systems within the Γ-point approximation was recently performed.[11] This is of particular interest when one would like a localized orbital picture within the framework of Car-Parrinello molecular dynamics (CPMD).

Here we reexamine the problem focusing on the Γ-point approximation only. For this case, Silvestrelli[12] has derived a formula for the spread in three dimensions for a molecular dynamics cell of arbitrary shape. The formula is based on the formulation of Marzari and Vanderbilt. Recently Resta has proposed a formula for the spread in one dimension which reduces to that of Marzari and Vanderbilt in the limit of large cell size.[13,14] We generalize Resta's formulation to three dimensions and arbitrary molecular dynamics cells. In addition we derive a formula for the spread and examine the convergence properties of these three different formulations.

Upon minimization of the spread functional the appropriate unitary transformation to the localized orbitals can be calculated. With explicit knowledge of the spread functional we can derive the complete expressions required to implement the iterative minimization procedure beyond a steepest descent scheme. The steepest descents method, used in Refs. 9, 11, and 12, performs reasonably for simple molecular systems, but it is known to have convergence problems when more complicated systems are analyzed. This can only be remedied by calculating the required gradient of the spread functional without any simplification, thus allowing the iterative calculation of maximally-localized orbitals with very efficient optimization schemes (e.g., conjugate gradient[15] and the direct inversion in the iterative subspace[16] method). Comparisons of the efficiency of the aforementioned optimization schemes to the steepest descents method and to the well known Jacobi optimization procedure is made.

The present methodology can be straightforwardly generalized to finite (nonperiodic) systems, thus providing a tool for Boys-Foster localization.[5] Furthermore we apply our optimization scheme also to the Pipek-Mezey localization[6] which is based on Mulliken population analysis.

II. DERIVATION OF THE FUNCTIONAL

We begin by reviewing the work of Resta.[14] In his treatment, the fundamental object for studying localization of an electronic state within Born-Von Karman boundary conditions is the dimensionless complex number,

$$z=\int_L dx\,\exp(i2\pi x/L)|\psi(x)|^2. \tag{1}$$

Here, L is the linear dimension, and $\psi(x)$ denotes the wave function. By considering the definition of the spread of the wave function to be $\Omega=\langle x^2\rangle-\langle x\rangle^2$, where $\langle\cdots\rangle$ denotes an expectation value, Resta has shown that to $O(1/L^2)$ the functional for the spread in one dimension to be

$$\Omega=\frac{1}{(2\pi)^2}\ln|z|^2. \tag{2}$$

One goal of this study is to generalize Eq. (1) to three dimensions and obtain the appropriate generalization of Eq. (2). Thus, we choose to study the following dimensionless complex number within Born-Von Karman boundary conditions:

$$z_I=\int_V d\mathbf{r}\,\exp(i\mathbf{G}_I\cdot\mathbf{r})|\psi(\mathbf{r})|^2. \tag{3}$$

Here, I labels a general reciprocal lattice vector, $\mathbf{G}_I=l_I\mathbf{b}_1+m_I\mathbf{b}_2+n_I\mathbf{b}_3$, where $\mathbf{b}_\alpha$ are the primitive reciprocal lattice vectors, the integers l, m, and n are the Miller indices, V is the volume of the supercell, and $\psi(\mathbf{r})$ denotes the wave function. We must find an appropriate function of the z_I's that gives the three dimensional spread in the case of an arbitrary simulation cell. We proceed by noting that in a molecular dynamics simulation the cell parameters (primitive lattice vectors) to describe systems of general symmetry are given by $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$. It is convenient to form a matrix of these cell parameters, $\overleftrightarrow{\mathbf{h}}=(\mathbf{a}_1,\mathbf{a}_2,\mathbf{a}_3)$ where the volume V of the simulation cell is given by the determinant of $\overleftrightarrow{\mathbf{h}}$. It is also very useful to define scaled coordinates, $\mathbf{s}=\overleftrightarrow{\mathbf{h}}^{-1}\cdot\mathbf{r}$ that lie in the unit cube. In molecular dynamics simulations, this allows one to perform periodic boundary conditions for systems with general symmetry by first transforming to the unit cube, performing cubic periodic boundary conditions, and transforming back to the general cell with the action of $\overleftrightarrow{\mathbf{h}}$.[17] One can also compute the reciprocal space vectors for systems of general symmetry with knowledge of the matrix of cell parameters. Thus the I th reciprocal lattice vector,

$$\mathbf{G}_I=2\pi(\overleftrightarrow{\mathbf{h}}^{-1})^{\mathrm{T}}\cdot\hat{\mathbf{g}}_I. \tag{4}$$

Here, the superscript T denotes transposition, and $\hat{\mathbf{g}}_I=(l_I,m_I,n_I)$ is the Ith Miller index. We then substitute this expression into Eq. (3) and use the definition of $\mathbf{s}$ to obtain,

$$z_I=\det\overleftrightarrow{\mathbf{h}}\int_0^1 d\mathbf{s}\,\exp(i2\pi\hat{\mathbf{g}}_I^{\mathrm{T}}\cdot\mathbf{s})|\psi(\overleftrightarrow{\mathbf{h}}\cdot\mathbf{s})|^2. \tag{5}$$

Note that the exponential in Eq. (5) is independent of any coordinate system. Following Resta[14] we can write the electron density in terms of a superposition of localized density and its periodic images, $|\psi(\overleftrightarrow{\mathbf{h}}\cdot\mathbf{s})|^2=\Sigma^{\infty}_{\hat{\mathbf{m}}=-\infty}n_{\mathrm{loc}}(\overleftrightarrow{\mathbf{h}}\cdot\mathbf{s}-\overleftrightarrow{\mathbf{h}}\cdot\mathbf{s}_0-\overleftrightarrow{\mathbf{h}}\cdot\hat{\mathbf{m}})$. Here $\hat{\mathbf{m}}$ is a vector of integers and $\overleftrightarrow{\mathbf{h}}\cdot\mathbf{s}_0$ is the center of the distribution such that $\int_{-\infty}^{\infty}d\mathbf{s}\,\overleftrightarrow{\mathbf{h}}\cdot\mathbf{s}\,n_{\mathrm{loc}}(\overleftrightarrow{\mathbf{h}}\cdot\mathbf{s})=0$. Using the Poisson summation formula,[18] we rewrite Eq. (5),

$$z_I=\exp(i2\pi\hat{\mathbf{g}}_I^{\mathrm{T}}\cdot\mathbf{s}_0)\hat{n}_{\mathrm{loc}}(-2\pi\hat{\mathbf{g}}_I^{\mathrm{T}}\cdot\overleftrightarrow{\mathbf{h}}^{-1}), \tag{6}$$

where $\hat{n}_{\mathrm{loc}}$ denotes the Fourier transform of n_{loc}. Furthermore, since we are considering n_{loc} to be localized, its Fourier transform is smooth over reciprocal distances and we can be assured that it is well represented about $\hat{g}_I=0$. We expand $\hat{n}_{\mathrm{loc}}(-2\pi\hat{\mathbf{g}}_I^{\mathrm{T}}\cdot\overleftrightarrow{\mathbf{h}}^{-1})$ to second order, obtaining

$$\hat{n}_{\mathrm{loc}}(-2\pi\hat{\mathbf{g}}_I^{\mathrm{T}}\cdot\overleftrightarrow{\mathbf{h}}^{-1})=1+\sum_{\alpha}\hat{g}_{\alpha,I}\left.\frac{\partial\hat{n}_{\mathrm{loc}}}{\partial\hat{g}_{\alpha,I}}\right|_{\hat{g}_I=0}+\frac{1}{2}\sum_{\alpha,\beta}\hat{g}_{\alpha,I}\hat{g}_{\beta,I}\left.\frac{\partial^2\hat{n}_{\mathrm{loc}}}{\partial\hat{g}_{\alpha,I}\partial\hat{g}_{\beta,I}}\right|_{\hat{g}_I=0}+\cdots. \tag{7}$$

The second term in Eq. (7) is zero given our imposed condition $\langle\overleftrightarrow{\mathbf{h}}\cdot\mathbf{s}\rangle=0$. Thus, we are left with

$$\hat{n}_{\mathrm{loc}}(-2\pi\hat{\mathbf{g}}_I^{\mathrm{T}}\cdot\overleftrightarrow{\mathbf{h}}^{-1})=1-\frac{(2\pi)^2}{2}V\sum_{\alpha,\beta}\hat{g}_{\alpha,I}\hat{g}_{\beta,I}\int_{-\infty}^{\infty}d\mathbf{s}\,s_\alpha s_\beta\;n_{\mathrm{loc}}(\overleftrightarrow{\mathbf{h}}\cdot\mathbf{s}). \tag{8}$$

Combining Eq. (8) and Eq. (6), we obtain

$$1-|z_I|=V\frac{(2\pi)^2}{2}\sum_{\alpha,\beta}\hat{g}_{\alpha,I}\hat{g}_{\beta,I}\int_{-\infty}^{\infty}d\mathbf{s}\,s_\alpha s_\beta n_{\mathrm{loc}}(\overleftrightarrow{\mathbf{h}}\cdot\mathbf{s}). \tag{9}$$

Keeping in mind that $\int_{-\infty}^{\infty}d\mathbf{s}\,\overleftrightarrow{\mathbf{h}}\cdot\mathbf{s}\,n_{\mathrm{loc}}(\overleftrightarrow{\mathbf{h}}\cdot\mathbf{s})=0$, one can define the spread of the electronic distribution for the case of a general box through

$$\langle r^2\rangle-\langle r\rangle^2=\langle(\overleftrightarrow{\mathbf{h}}\cdot\mathbf{s})^2\rangle=\sum_{\alpha,\beta}g_{\alpha\beta}V\int_{-\infty}^{\infty}d\mathbf{s}\,s_\alpha s_\beta\,n_{\mathrm{loc}}(\overleftrightarrow{\mathbf{h}}\cdot\mathbf{s}). \tag{10}$$

Here, $g_{\alpha\beta}=\Sigma_\mu\overleftrightarrow{h}^{\mathrm{T}}_{\alpha\mu}\overleftrightarrow{h}_{\mu\beta}$ can be thought of as a metric tensor to describe the corresponding distances in the unit cube. Equation (10) shows us exactly how the length scales are built into the spread through the metric tensor. From direct comparison of Eq. (9) and Eq. (10) we see that for supercells of general symmetry we need to choose linear combinations of $\hat{g}_{\alpha,I}\hat{g}_{\beta,I}$ that reproduce the metric tensor, $g_{\alpha\beta}$. However, as stated earlier, $\hat{g}_{\alpha,I}$ are dimensionless numbers. Thus, an appropriate generalization takes the form of a sum rule,

$$g_{\alpha\beta}=\sum_I\omega_I\hat{g}_{\alpha,I}\hat{g}_{\beta,I}. \tag{11}$$

Here, ω_I are the ''weights'' with the appropriate dimensions to be determined in Appendix A. Thus, it should also be clear that $g_{\alpha\beta}$ will have at most six independent entries (for triclinic symmetry) and thus a maximum of six weights are needed. It is interesting to note that by multiplying Eq. (11) on the left and right hand sides by $\overleftrightarrow{\mathbf{h}}^{-1}$ and using the definition of $\mathbf{G}_I$, one will recover the rule used by Silvestrelli[12] and by Marzari and Vanderbilt.[9] Finally, we generalize to more than one state, $|\psi\rangle\rightarrow|\psi_n\rangle$ and the desired expression for the spread, Ω in a supercell of general symmetry is

$$\Omega = \frac{2}{(2\pi)^2} \sum_n^{\mathrm{N_{states}}} \sum_I \omega_I (1 - |z_{I,n}|) + O((2\pi \hat{\mathbf{g}}_I^{\mathrm{T}} \cdot \overleftrightarrow{\mathbf{h}}^{-1})^2),$$

$$z_{I,n} = \int_V d\mathbf{r}\, \exp(i\mathbf{G}_I \cdot\ \mathbf{r}) |\psi_n(\mathbf{r})|^2, \tag{12}$$

where Eq. (11) determine the $\mathbf{G}_I$'s.

At this point it is useful to make contact with other spread formulas that are present in the current literature. Following Resta's derivation one finds the formula,[14] that in our notation reads

$$\Omega = -\frac{1}{(2\pi)^2} \sum_n^{\mathrm{N_{states}}} \sum_I \omega_I \log |z_{I,n}|^2, \tag{13}$$

with $z_{I,n}$ defined as above. Equation (13) is obtained by inserting Eq. (8) into Eq. (6), taking the log of the absolute value and expanding to consistent order.

Silvestrelli[12] on the other hand uses (again, in our notation)

$$\Omega = \frac{1}{(2\pi)^2} \sum_n^{\mathrm{N_{states}}} \sum_I \omega_I (1 - |z_{I,n}|^2), \tag{14}$$

with a similar defininition for $z_{I,n}$. Obviously, Eq. (14) is obtained from Eq. (13) by an expansion of the log.

At first glance, it seems confusing that there are different definitions for the spread. Admittedly, one has to keep in mind that all formulas are only valid up to the order given in Eq. (12). Thus, although different, they are consistent and there is no fundamental reason to choose one definition of the spread over another. Consequently, we compare in Sec. IV the spreads of various model systems using all different definitions.

One can also derive a general expression for the expectation value of the periodic position operator for computing the center of the localized function. Recall that for a cubic simulation supercell the expectation value of the position operator is given as

$$r_{\alpha,n} = -\frac{L}{2\pi} \operatorname{Im} \log z_{\alpha,n},$$

$$z_{\alpha,n} = \int_V d\mathbf{r}\, \exp(i\hat{\mathbf{g}}_\alpha \cdot \mathbf{r}) |\psi_n(\mathbf{r})|^2, \tag{15}$$

where $\hat{\mathbf{g}}_1 = (1,0,0)$, $\hat{\mathbf{g}}_2 = (0,1,0)$, and $\hat{\mathbf{g}}_3 = (0,0,1)$, and Im denotes the imaginary part. Again, the salient feature of Eq. (15) is that the expectation value of the exponential is invariant with respect to the choice of cell. Thus, a general equation for the expectation value of the position operator in supercells of arbitrary symmetry is

$$r_{\alpha,n} = -\sum_\beta \frac{\overleftrightarrow{h}_{\alpha\beta}}{2\pi} \operatorname{Im} \log z_{\alpha,n}. \tag{16}$$

Having established the definition of the spread formulas in the context of WF's we proceed with a detailed description of their computation.

III. A GENERALIZED LOCALIZATION PROCEDURE

The mathematical problem which defines the localization procedure is to find the unitary transformation, U, on the orbitals,

$$|\tilde{\psi}_n\rangle = \sum_i U_{in} |\psi_i\rangle, \tag{17}$$

that simultaneously minimizes the spread functional, Ω. To present a general formulation it is convenient to work with a generalized form

$$\Omega = \sum_n \sum_I f(|z_{I,n}|^2),$$

$$z_{I,n} = \langle \psi_n | O^I | \psi_n \rangle, \tag{18}$$

where f and O^I denote an appropriate function and operator.

If we neglect the weights and constants in favor of simplicity, we obtain the different spread functionals of the last section, defined through Eq. (12), Eq. (13), and Eq. (14) by setting

$$O^I = \exp(i\mathbf{G}_I \cdot \mathbf{r})$$

$$f_1(|z_{I,n}|^2) = \sqrt{|z_{I,n}|^2} = |z_{I,n}|,$$

$$f_2(|z_{I,n}|^2) = \log(|z_{I,n}|^2),$$

$$f_3(|z_{I,n}|^2) = |z_{I,n}|^2. \tag{19}$$

The values of index I will range at most from one to six. It is important to notice that maximizing Eq. (18) is equivalent to minimizing the spread functional.

At this point it is useful to make the connection with methods used in traditional applications of quantum chemistry. Due to its general form, Eq. (18) is also suited for finite systems. The Boys-Foster and the Pipek-Mezey method,[5,6] which are widely used to obtain localized molecular orbitals (MO) in quantum chemistry, can both be formulated by working with f_3. Using MO's instead of BO's we define the operator, O^I, in Eq. (19) for the Boys-Foster and Pipek-Mezey scheme, respectively, as

$$O^I = r_I \quad \text{or} \quad O^J = \sum_{\mu \in J} \frac{1}{2} \{ |\tilde{\mu}\rangle\langle\mu| + |\mu\rangle\langle\tilde{\mu}| \}. \tag{20}$$

Here, r_I denotes the conventional position operator, runs from one to three, J runs from one to the number of atoms, $\{|\mu\rangle, \mu \in J\}$ denotes the atomic basis set of atom J, and $|\tilde{\mu}\rangle = \Sigma_\nu S^{-1}_{\nu\mu} |\nu\rangle$, where S is the overlap matrix of the atomic basis set.

While the Boys-Foster method minimizes the total spread, $\Omega = \langle r^2 \rangle_n - \langle r \rangle_n^2$ (and hence maximizes $\langle r \rangle_n^2$),[5] the Pipek-Mezey method is different and warrants some explanation. The projection operator in Eq. (20) used by Pipek and Mezey (PM) is closely related to the Mulliken population analysis.[6] In fact, maximizing the PM functional corresponds to a minimization of the number of atoms over which an orbital is spread. The popularity of the PM functional originates from two sources. First, it is very easy to implement and leads to a fast algorithm when combined with the linear combination of atomic orbitals method. Second, the PM functional, unlike the Boys-Foster method, preserves the σ-π separation of double bonds. This picture of double bonds is in chemistry usually preferred over the τ (banana) bond picture generated by the Boys-Foster localization procedure.

The actual calculation of maximally localized WF's or maximally localized MO's within our localization procedure is relatively simple. First, we take the output of a conventional electronic structure calculation (BO's in the periodic, MO's in the finite case), choose a spread functional and solve for the unitary transformation producing the orbitals that maximize Eq. (18). As stated earlier, we have two choices of spread functionals for finite systems and three choices of spread functionals for periodic systems. The details of the calculation are described in the following.

One must now focus on the computation of U. To ensure a maximally localized function, we would like to find an efficient solution to

$$\frac{\partial\Omega}{\partial U_{ij}}=0, \tag{21}$$

where U is considered to be real since we are working within the $\mathbf{\Gamma}$-point approximation. There are two principal alternatives for parametrizing the unitary transformation, U, first as a direct product of elementary plane rotations, and second as the exponential of an antisymmetric matrix. The first parametrization scheme, discussed in the next subsection, amounts to the well known Jacobi optimization procedure for finding eigenvalues of general matrices. The second parametrization choice of U, used in our method, is based on the exponential alternative as investigated in Sec. III B.

A. Orbital rotations

The traditional method in quantum chemistry for computing localized MO's is the method of two-by-two orbital rotations first introduced by Edmiston and Ruedenberg.[7] The basic idea of the method is to tackle the problem of finding U by performing a sequence of consecutive two-by-two rotations among all pairs of orbitals. The elementary step consists of a plane rotation where two orbitals i and j are rotated through an angle, ϕ. To proceed we select an optimal angle to ensure that our spread functional, as defined in Eq. (18), is iteratively maximized. The transformed expectation values are denoted with $\tilde{z}_{I,i/j}$ and are obtained as

$$\tilde{z}_{I,i}=\cos(\phi)z_{I,i}+\sin(\phi)z_{I,j},$$

$$\tilde{z}_{I,j}=-\sin(\phi)z_{I,i}+\cos(\phi)z_{I,j}. \tag{22}$$

Thus, combining Eq. (22) with Eq. (18) it is straightforward to calculate the change in the functional value, $\Delta\Omega$ as a function of ϕ. The most natural way to obtain the optimal angle which maximizes the change in the functional value is to compute the derivative of $\Delta\Omega$ with respect to ϕ, set it to zero and solve for ϕ. This is precisely the way the method of orbital rotations is implemented and an explicit calculation yields

$$\tan(4\phi)=-\frac{a}{b},$$
$$a=\mathrm{Re}[M_{ij}(\overline{M}_{ii}-\overline{M}_{jj})],\quad b=|M_{ij}|^2-\frac{1}{4}|M_{ii}-M_{jj}|^2, \tag{23}$$

where $M_{ij}=\Sigma_I z_{I,ij}$ and Re denotes the real part. $\phi+n\pi/4$, $n\in\mathbb{Z}$ are the solutions of Eq. (23) corresponding to maxima and minima. For a maximum the condition, $\partial^2\Delta\Omega/\partial\phi^2=16b\cos(4\phi)-16a\sin(4\phi)<0$ has to be fulfilled.

Unfortunately there is one severe restriction. Equation (23) is only valid in the case, $f_3(x)=x$, namely in connection with the Silvestrelli-Marzari-Vanderbilt, the Boys and the Pipek-Mezey functional (see Sec. III B). In the other cases, $f_1(x)=\sqrt{x}$ (functional of the present work) and $f_2(x)=\log(x)$ (Resta), no analogous formula is derivable. The reason is that the explicit solution of $\partial\Delta\Omega/\partial\phi=0$ with respect to ϕ seems not analytically tractable. Nevertheless, one can still implement the method of orbital rotations in the above cases by a numerical maximization of $\Delta\Omega$ as a function of ϕ using derivative information.

B. Exponential representation

The ansatz, $|\tilde{\psi}_n\rangle=\Sigma_i U_{in}|\psi_i\rangle$, where U is a unitary matrix, leads to the transformed expectation value

$$\tilde{z}_{I,n}=\sum_{ij} U^T_{in}U_{jn}z_{I,ij}, \tag{24}$$

with $z_{I,ij}=\langle\psi_i|O^I|\psi_j\rangle$. As discussed above, we parametrize $U=\exp(A)$ as the exponential of an antisymmetric matrix and calculate the gradient with respect to A. Using the chain rule the gradient splits into two pieces,

$$\frac{\partial\Omega}{\partial A_{ij}}=\sum_{st}\frac{\partial\Omega}{\partial U_{st}}\frac{\partial U_{st}}{\partial A_{ij}}=\sum_{I,n}\sum_{st}\frac{\partial f(|z_{I,n}|^2)}{\partial U_{st}}\frac{\partial U_{st}}{\partial A_{ij}}. \tag{25}$$

It is worthwhile to note that only the first piece depends on the type of spread functional and its evaluation is straightforward,

$$\begin{aligned}\frac{\partial f(|z_{I,n}|^2)}{\partial U_{st}}&=f'(|z_{I,n}|^2)\frac{\partial|z_{I,n}|^2}{\partial U_{st}}\\&=2f'(|z_{I,n}|^2)\left(\sum_i U^T_{in}\delta_{tn}z_{I,is}\right)\\&\quad\times\left(\sum_{kl}U^T_{kn}U_{ln}\overline{z}_{I,kl}\right)+\text{c.c.},\end{aligned} \tag{26}$$

where $\overline{z}$ denotes the complex conjugate (c.c.) of z and f' is the derivative of f. Combining Eq. (25) and Eq. (26) a general form for the gradient is obtained as

$$\frac{\partial\Omega}{\partial A_{ij}}=\sum_{st}M_{st}\frac{\partial U_{st}}{\partial A_{ij}}=\mathrm{Tr}\left[M^T\frac{\partial U_{st}}{\partial A_{ij}}\right], \tag{27}$$

where M is defined via Eq. (26). However, the Pipek-Mezey functional has to be treated with special care. Since the summation index, I runs from one to the number of atoms of the system, one has to use the separability of the corresponding operator, O^I to calculate M in an efficient way.

The calculation of $\partial U_{st}/\partial A_{ij}$ is more subtle. We have to calculate the derivative of a matrix function, here the exponential function, $U=\exp(A)$ with respect to A. This can be done by writing the matrix function in an alternative way using a complex contour integral,[19]

$$\begin{aligned}\frac{\partial U}{\partial A_{ij}}&=\frac{\partial\ \exp(A)}{\partial A_{ij}}\\&=\frac{1}{2\pi i}\frac{\partial}{\partial A_{ij}}\oint \exp(z)(z\underline{1}-A)^{-1}dz\\&=\frac{1}{2\pi i}\oint \exp(z)(z\underline{1}-A)^{-1}(1^{ij}-1^{ji})(z\underline{1}-A)^{-1}dz\\&=R^{\dagger}\frac{1}{2\pi i}\oint \exp(z)(z\underline{1}-\Lambda)^{-1}R(1^{ij}-1^{ji})\\&\quad\times R^{\dagger}(z\underline{1}-\Lambda)^{-1}dzR.\end{aligned}\tag{28}$$

$\underline{1}$ denotes the identity matrix, $(1^{ij})_{kl}=\delta_{ki}\delta_{lj}$, R is the eigenvector matrix of A with eigenvalues λ_k and $\Lambda_{kl}=\lambda_k\delta_{kl}$. Carrying out the integration over z, one obtains

$$\frac{1}{2\pi i}\oint\frac{\exp(z)}{(z-\lambda_k)(z-\lambda_l)}dz=\begin{cases}e^{\lambda_k}, & \lambda_k=\lambda_l\,,\\ \dfrac{e^{\lambda_k}-e^{\lambda_l}}{\lambda_k-\lambda_l}, & \lambda_k\neq\lambda_l\,.\end{cases}\tag{29}$$

Performing some simple algebraic transformations, Eq. (27) becomes

$$\begin{aligned}\frac{\partial\Omega}{\partial A_{ij}}&=\mathrm{Tr}[M^TR^{\dagger}\{C^{ij},B\}R]\\&=(R^{\dagger}\{RM^TR^{\dagger},B\}R)_{ji}-(R^{\dagger}\{RM^TR^{\dagger},B\}R)_{ij}\,,\end{aligned}\tag{30}$$

where the B_{kl} components are defined through Eq. (29), $\{C^{ij},B\}$ denotes a component-wise matrix multiplication and $C^{ij}=R(1^{ij}-1^{ji})R^{\dagger}$. The final transformation in Eq. (30) is verified by inserting the explicit definition of the matrix 1^{ij}.

Using the results above we have now a very useful scheme to optimize Ω by iterating the following steps.

Start with an arbitrary matrix, e.g., $A=0$.

Diagonalize A to obtain the eigenvector matrix R and the diagonal matrix Λ with the eigenvalues as diagonal elements.

Calculate the unitary matrix via $U=\exp(A)=R^{\dagger}e^{\Lambda}R$.

Compute M and B defined in Eq. (27), respectively, Eq. (29).

Calculate the gradient according to Eq. (30).

Update A and repeat process.

Within the above scheme the desired gradient is obtained analytically and we are able to combine our iterative localization procedure with gradient methods developed to accelerate convergence.

In addition we have calculated a simplified expression for the second derivative to be used as a preconditioner for a further speed up of the iterative localization (see Appendix B). There we also compute the gradient at $A=0$ which is equivalent to the gradient used by Sivestrelli *et al.*[11,12] Section IV is devoted to a detailed comparison of the methods presented in this section.

IV. RESULTS AND DISCUSSION

The iterative localization algorithm, presented in this work, has been implemented in a hybrid Gaussian and plane wave (PW) density functional scheme[20] and in the CPMD code[21] which is based on a plane wave expansion. Both programs are suited for periodic and for finite systems.

One of the goals of our work is to make a comparison of the different spread functionals proposed in the literature, including the one derived in this work for supercells of general symmetry. In order to perform a comparison, we have chosen a simple system which has been previously studied using different spread functionals. Thus, we consider the case of one isolated water molecule periodically replicated in different supercell symmetries (simple cubic, orthorhombic, hexagonal, fcc, bcc, hexagonal, and triclinic) where the same cell volume is maintained.[22] It is clear that the centroid of the localized functions [Eq. (16)] should remain in the same positions relative to the atoms for all supercells considered (ignoring the negligible effects of distortion from the periodic images for the cell parameters chosen). Following the work of Ref. 12 we use the general form of the functional [Eq. (18)], and specifically the spread functionals given by Eqs. (12), (13), and (14) for the iterative maximization.

Table I reports our results for the distances between the oxygen atom and the centroids of the four different WF's [calculated using Eq. (16)], and the spreads for the different supercell symmetries. No systematic differences in the distances are recognizable. Besides numerical noise, all considered spread functionals lead, independent from the choice of the supercell, to the same position of the centroids relative to the oxygen atom. This fact is in contrast to the calculated spread, here the distinct definitions result in slightly different values, even though one finds qualitative agreement.

After having compared our functional to previous work in literature, we examine possible ways to improve the iterative localization beyond a simple steepest descent scheme. To achieve a faster convergence the following optimization methods, in connection with the scheme described in Sec. III are implemented.

A steepest descent (SD) with line search procedure performed in the following way. After bracketing the maximum, a parabolic fit through three points is carried out. The SD serves as a benchmark, since one can combine the method also with the approximate gradient [Eq. (B1)].

The Polak-Ribière conjugate gradient method (CG).[15]

The Polak-Ribière conjugate gradient method in combination with a preconditioner (CG+PR). Close to the maximum we replace the pure gradient $\mathbf{g}$ by $H^{-1}\mathbf{g}$ where H^{-1} denotes the inverse of the approximate diagonal Hessian matrix calculated via Eq. (B1).

The direct inversion in the iterative subspace method[16] (DIIS) in combination with a preconditioner. In addition the

TABLE I. Distances, with respect to the position of the oxygen ion, and spreads of the two covalent orbital WF's ($d_{C1/2}$ and $\Omega_{C1/2}$ in Å) and the two lone-pair WF's ($d_{L1/2}$ and $\Omega_{L1/2}$ in Å) of the isolated water molecule . Data have been computed for different supercell symmetries, using the functional of present work [PW, Eq. (12)], the Resta functional [R, Eq. (13)], and the Silvestrelli-Marzari-Vanderbilt functional [SMV, Eq. (14)]. For details see text.

Symmetry	Functional	d_{C1}	Ω_{C1}	d_{C2}	Ω_{C2}	d_{L1}	Ω_{L1}	d_{L2}	Ω_{L2}
Simple cubic	PW	0.53	0.72	0.53	0.72	0.30	0.75	0.30	0.75
	R	0.53	0.72	0.53	0.72	0.30	0.76	0.30	0.76
	SMV	0.53	0.71	0.53	0.71	0.30	0.75	0.30	0.75
Orthorhombic	PW	0.53	0.72	0.53	0.72	0.30	0.75	0.30	0.75
	R	0.53	0.72	0.53	0.72	0.31	0.76	0.30	0.76
	SMV	0.54	0.71	0.53	0.71	0.30	0.75	0.30	0.75
fcc	PW	0.54	0.71	0.53	0.71	0.30	0.75	0.30	0.74
	R	0.53	0.72	0.53	0.72	0.30	0.76	0.30	0.75
	SMV	0.54	0.70	0.54	0.70	0.30	0.74	0.30	0.73
bcc	PW	0.53	0.73	0.53	0.72	0.31	0.77	0.30	0.76
	R	0.53	0.73	0.53	0.72	0.30	0.78	0.30	0.76
	SMV	0.53	0.73	0.53	0.72	0.30	0.77	0.29	0.76
Hexagonal	PW	0.53	0.74	0.53	0.72	0.31	0.78	0.30	0.77
	R	0.53	0.73	0.53	0.72	0.30	0.78	0.30	0.76
	SMV	0.54	0.74	0.53	0.72	0.31	0.78	0.30	0.77
Triclinic	PW	0.53	0.71	0.53	0.71	0.31	0.75	0.30	0.75
	R	0.53	0.72	0.53	0.72	0.30	0.76	0.30	0.76
	SMV	0.54	0.71	0.53	0.71	0.30	0.75	0.30	0.75

diagonal approximation of the Hessian matrix is improved by making use of the information gained by calculating exact first derivatives at a series of iteration points. In our implementation the limited memory–BFGS method[23] is used which directly updates the inverse of the Hessian matrix.

Method of orbital rotations (OR) as discussed in Sec. III A.

To study the effect of the different optimization methods on the convergence of our scheme we consider four periodic systems, using the functional proposed in this work [PW, Eq. (12)], the Resta functional [R, Eq. (13)], and the Silvestrelli-Marzari-Vanderbilt functional [SMV, Eq. (14)] and five finite systems using the Pipek-Mezey (PM) and the Boys-Foster (BF) functional. As finite systems we have chosen the formaldehyde derivate formamide $CHONH_2$ (9), the alkane pentane C_5H_{12} (16), the aromate naphthalene $C_{10}H_8$ (24), the amino acid histidine $C_6H_9N_3O_2$ (30) and the steroid testosterone $C_{19}H_{28}O_2$ (58). As periodic benchmark systems serve bulk silicon Si_8 (16), bulk water $(H_2O)_8$ (32), diamond C_{32} (64) and β-Cristobalite $(SiO_2)_{16}$ (128). The number of doubly occupied orbitals is added in parentheses. The criterion used to classify the properties of a given method is as follows, we have always maintain the same accuracy in convergence and only evaluate the number of steps required to reach this.

The results of our calculation are summarized in Table II for the finite and in Table III for the periodic systems. Obviously there is a wide range in convergence behavior depending on the system size but also on the specific chemical properties. Small, fully saturated systems are easy to localize (Si_8,C_5H_{12}) and in those cases a steepest descent scheme is sufficient. However, this is no longer true if one switches to more complicated systems including electron lone pairs, double bonds or aromatic rings in connection with an increasing number of orbitals. In these cases, a considerable gain is obtained using high level optimization methods (CG, CG+PR, DIIS). For the biggest system we have studied, more than an order of magnitude increase in convergence speed is observed compared to the steepest descent with line search procedure. On the other hand the OR scheme, in spite of its simplicity, is remarkably efficient.[24]

It is not surprising that the more sophisticated iterative schemes are more efficient than the steepest descent procedure. However, for cases where one would like the WF's not only for the final configuration, but for evenly sampled times along the trajectory, an efficient scheme is imperative.

One last comment is in order. We find the best convergence using the preconditioned DIIS scheme. Unfortunately, the method converges to the ''closest'' stationary point which in many cases is not the global maxima. Thus, it seems more advantageous to work in a practical implementation with the CG+PR method.

TABLE II. Number of iteration steps to reach convergence for different optimization methods. Convergence is assumed if the relative value of the spread functional is decreasing by less than 10^{-8} for successive iteration steps. The considered methods are a steepest descent (SD) with line search procedure, the Polak-Ribière conjugate gradient method (CG), the Polak-Ribière conjugate gradient method with a preconditioner (CG+PR), the direct inversion in iterative subspace method (DIIS) with a preconditioner, and the orbital rotation method (OR). One step of OR is about three times more expensive in CPU time compared to the other methods. B denotes the Boys, PM the Pipek-Mezey functional. The number of double occupied orbitals of the respective system is added in parentheses.

Functional	SD	CG	CG+PR	DIIS	OR
		Formamide (9)			
BF	394	62	52	48	19
PM	187	39	36	30	24
		Pentane (16)			
BF	57	26	25	24	34
PM	26	18	15	16	30
		Naphtalene (24)			
BF	614	104	76	75	62
PM	172	47	39	31	58
		Histidine (30)			
BF	2036	182	156	117	77
PM	365	90	70	66	66
		Testosterone (58)			
BF	1444	236	202	122	152
PM	567	77	73	54	160

TABLE III. Number of iteration steps to reach convergence for different optimization methods. Convergence is assumed if the relative value of the localization functional is decreasing by less than 10^{-8} for successive iteration steps. The considered methods are a steepest descent (SD) with line search procedure, the Polak-Ribière conjugate gradient method (CG), the Polak-Ribière conjugate gradient method with a preconditioner (CG+PR), the direct inversion in iterative subspace method (DIIS) with a preconditioner, and the method of orbital rotations (OR). One step of OR is about three times more expensive in CPU time compared to the other methods. PW denotes the functional of present work [Eq. (12)], R the Resta functional [Eq. (13)], and SMV the Silvestrelli-Marzari-Vanderbilt functional [Eq. (14)]. The number of double occupied orbitals of the respective system is added in parentheses.

Function	SD	CG	CG+PR	DIIS	OR
		Si_8 (16)			
PW	28	19	19	19	25
R	29	19	19	19	37
SMV	28	19	18	18	32
		$(H_2O)_8$ (32)			
PW	323	60	44	42	67
R	740	89	72	61	92
SMV	248	71	61	53	87
		C_{32} (64)			
PW	216	52	38	32	109
R	301	73	66	52	141
SMV	197	57	39	35	184
		$(SiO_2)_{16}$ (128)			
PW	5199	479	253	178	261
R	8634	2932	478	394	307
SMV	3348	415	210	172	375

V. CONCLUSIONS

We have generalized the work of Resta to three dimensions to derive a spread functional as a starting point to calculate maximally-localized Wannier functions in simulation cells of general symmetry suitable for periodic systems in the **Γ**-point approximation. Thus, one can easily perform a calculation in a supercell with arbitrary symmetry with knowledge of only the cell parameters.

The functional turns out to be equivalent to others discussed in the literature, it differs, besides its more general form, only in the higher-order terms from either the Silvestrelli-Marzari-Vanderbilt or Resta proposals.

In addition, we have derived an iterative scheme to obtain maximally-localized orbitals. The method is also suited for finite systems and combination with very efficient optimization procedures is possible.

To compare the efficiency of our approach with the standard method in quantum chemistry proposed by Edmiston and Ruedenberg,[7] we generalize the method of orbital rotations to a wider class of spread functionals.

Test calculation show that with increasing system size and chemical complexity the use of high level optimization methods lead to a considerably faster convergence, for the biggest systems the performance is improved by more than a factor of ten. On the other hand, the simple orbital rotation scheme is surprisingly efficient. With respect to an practical implementation both methods have advantages, the orbital rotation method is easier to implement, nevertheless the efficiency is fairly good, our method is more general by being, at least for larger systems, clearly faster.

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APPENDIX A: DETERMINATION OF THE WEIGHTS

In this appendix we determine the weights, ω_I as defined in the sum rule Eq. (11) for supercells of general symmetry. Recall that the metric $\overleftrightarrow{\mathbf{g}}$ will contain at most six independent entries as defined by the case of least symmetry, triclinic. Thus, Eq. (11) is a linear set of six equations with six unknowns. We have freedom to choose the six Miller indices, $\hat{\mathbf{g}}_I$ of which we are to take the linear combinations. For computational convenience of computing z_I we choose the first six indices that take you from one to the next point in the Brillouin zone. Namely, $\hat{\mathbf{g}}_1=(1,0,0)$, $\hat{\mathbf{g}}_2=(0,1,0)$, $\hat{\mathbf{g}}_3=(0,0,1)$, $\hat{\mathbf{g}}_4=(1,1,0)$, $\hat{\mathbf{g}}_5=(1,0,1)$, $\hat{\mathbf{g}}_6=(0,1,1)$. With this choice of $\hat{\mathbf{g}}_I$ the explicit system of equations based on Eq. (11) takes the following simple form:

$$\begin{pmatrix} 1 & 0 & 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 1 & 1 \end{pmatrix} \begin{pmatrix} \omega_1 \\ \omega_2 \\ \omega_3 \\ \omega_4 \\ \omega_5 \\ \omega_6 \end{pmatrix} = \begin{pmatrix} g_{11} \\ g_{12} \\ g_{13} \\ g_{22} \\ g_{23} \\ g_{33} \end{pmatrix}. \tag{A1}$$

Thus, the solution to Eq. (A1) yields the following set of general weights:

$$\begin{aligned} \omega_1 &= g_{11} - g_{12} - g_{13}, \\ \omega_2 &= g_{22} - g_{12} - g_{23}, \\ \omega_3 &= g_{33} - g_{13} - g_{23}, \\ \omega_4 &= g_{12}, \\ \omega_5 &= g_{13}, \\ \omega_6 &= g_{23}. \end{aligned} \tag{A2}$$

Equation (A2) indeed reduces to the specific cases computed in Ref. 12. However, here, the case for triclinic symmetry is also included. Thus, with knowledge of the cell parameters, in conjunction with Eq. (12) allows one to compute the maximally localized WF.

APPENDIX B: APPROXIMATE EXPRESSIONS FOR THE GRADIENT AND THE SECOND DERIVATIVE

We can also calculate the second derivative analytically by the same methods as described in Sec. III. However, for our purposes an approximate solution is sufficient. The simplest approximation is to neglect all off-diagonal elements, thus allowing for an easy matrix inversion as needed in optimization schemes. This approximation is justified near the maximum where the Hessian matrix is diagonal dominant.

Further we can calculate the diagonal elements in an approximate way too. Using a power series expansion of the exponential function and exchanging limit and summation, it is easy to show that $\lim_{A\to 0}\exp(\pm A)=1$, $\lim_{A\to 0}\partial\exp(\pm A)/\partial A_{ij}=\pm(1^{ij}-1^{ji})$, and $\lim_{A\to 0}\partial^2\exp(\pm A)/\partial A_{ij}^2=(1^{ij}-1^{ji})^2=-(1^{ii}+1^{jj})$. With this we get

$$\begin{aligned} \lim_{A\to 0}\frac{\partial^2\Omega}{\partial A_{ij}^2} = -4\sum_I \left(|z_{I,i}|^2 f'(|z_{I,i}|^2) + |z_{I,j}|^2 f'(|z_{I,j}|^2)\right) \\ + 16\sum_I \left(\mathrm{Re}[z_{I,ij}\overline{z_{I,j}}]^2 f''(|z_{I,j}|^2)\right. \\ \left. + \mathrm{Re}[z_{I,ij}\overline{z_{I,i}}]^2 f''(|z_{I,i}|^2)\right), \end{aligned} \tag{B1}$$

ending up with an expression for the second derivative in the limiting case, $A\to 0$. In order to use Eq. (B1), we first perform an optimization until close to the maximum, then we update the expectation values via Eq. (24) and restart the iteration with $A=0$. At that point Eq. (B1) is a reasonable estimate of the diagonal elements of the second derivative and we can use the inverse of the approximate diagonal matrix as a preconditioner.

We can also calculate the gradient in the same limit,

$$\begin{aligned} \lim_{A\to 0}\frac{\partial\Omega}{\partial A_{ij}} = 4\sum_I \left(\mathrm{Re}[z_{I,ij}\overline{z_{I,j}}] f'(|z_{I,j}|^2)\right. \\ \left. - \mathrm{Re}[z_{I,ij}\overline{z_{I,i}}] f'(|z_{I,i}|^2)\right). \end{aligned} \tag{B2}$$

Equation (B2) amounts to the gradient used by Sivestrelli *et al.*[11,12] for general functionals. In each iteration step one has to update the expectation values via Eq. (24) and to restart with $A=0$. This amounts to a redefinition of the optimization parameters, making the use of global schemes impossible. In addition, to update the expectation values means to diagonalize A in order to obtain the unitary matrix, $U = \exp(A)$. Since the diagonalization is also the most time consuming step in the calculation of the full gradient, the use of Eq. (30) is in any case advantageous.

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0.0, 15.9), $\mathbf{a}_2=(0.0,\ 15.9,\ 15.9)$, $\mathbf{a}_3=(-15.9,\ 15.9,\ 0.0)$; bcc: $\mathbf{a}_1=(12.6,\ 12.6,\ 12.6)$, $\mathbf{a}_2=(-12.6,\ 12.6,\ 12.6)$, $\mathbf{a}_3=(-12.6,\ -12.6,\ 12.6)$; hexagonal: $\mathbf{a}_1=(20.0,\ 0.0,\ 0.0)$, $\mathbf{a}_2=(-10.0,\ 17.3,\ 0.0)$, $\mathbf{a}_3=(0.0,\ 0.0,\ 23.1)$; triclinic: $\mathbf{a}_1=(20.0,\ 0.0,\ 0.0)$, $\mathbf{a}_2=(7.2,\ 22.9,\ 0.0)$, $\mathbf{a}_3=(1.8,\ 3.2,\ 17.6)$.

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