Direct Unconstrained Variable-Metric Localization of One-Electron Orbitals

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ABSTRACT: Spatially localized one-electron orbitals, orthogonal and non-orthogonal, are widely used in electronic structure theory to describe chemical bonding and speed up calculations. In order to avoid linear dependencies of localized orbitals, the existing localization methods either constrain orbital transformations to be unitary, that is, metric preserving, or, in the case of variable-metric methods, fix the centers of non-orthogonal localized orbitals. Here, we developed a different approach to orbital localization, in which these constraints are replaced with a single restriction that specifies the maximum allowed deviation from the orthogonality for the final set of localized orbitals. This reformulation, which can be viewed as a generalization of existing localization methods, enables one to choose the desired balance between the orthogonality and locality of the orbitals. Furthermore, the approach is conceptually and practically simple as it obviates the necessity in unitary transformations and allows one to determine optimal positions of the centers of non-orthogonal orbitals in an unconstrained and straightforward minimization procedure. It is demonstrated to produce well-localized orthogonal and non-orthogonal orbitals with the Berghold and Pipek–Mezey localization functions for a variety of molecules and periodic materials including large systems with nontrivial bonding.

INTRODUCTION

Spatially localized orbitals are of paramount importance in one-electron theories such as the Hartree–Fock method and Kohn–Sham density functional theory as well as in post-Hartree–Fock wave function-based electron-correlation methods. Localized orbitals are widely used to describe and visualize chemical bonding between atoms, thus helping classify bonds and understand electronic-structure origins of observed properties of atomistic systems. Furthermore, localized orbitals are the key ingredient in multiple local electronic-structure methods that dramatically reduce the computational cost of modeling electronic properties of large systems. Spatially localized orbitals are known as localized molecular orbitals (LMOs) in the field of molecular quantum chemistry and maximally localized Wannier functions (MLWFs) in solid state physics and materials science. Here, they will be collectively referred to as LMOs, whereas the eigenstates of the effective one-electron Hamiltonian will be called canonical molecular orbitals (CMOs) regardless of whether the system is isolated or treated with periodic boundary conditions.

In traditional localization methods, LMOs are constructed by finding a unitary transformation of CMOs that minimizes a localization function that effectively measures the spread of individual orbitals. Since CMOs are orthogonal and a unitary transformation preserves the orbital metric, LMOs obtained in this way are orthogonal (OLMOs) by construction. Multiple localization functions have been proposed for molecular systems including Boys–Foster, Edmiston–Ruedenberg, Pipek–Mezey, and von Niessen. The Boys–Foster localization is perhaps the most popular because of the simplicity of its physical interpretation, low computational complexity, and ease of implementation. The Pipek–Mezey localization, which maximizes atomic charges of each orbital, is also widely used because it does not mix LMOs representing $\sigma$ and $\pi$ bonds and thus gives a clear picture of bonding patterns. In the past decade, these well-established localization functions have been modified to reduce orbital tails and produce more uniform localization across the set of LMOs. For large supercells of condensed-phase periodic systems, where electronic structure can be described with the $\Gamma$-point sampling of the Brillouin zone, several efficient optimization methods have been proposed to construct MLWF. While the methods listed above rely on different localization criteria, they have been formulated to ensure that orbitals remain orthogonal in a localization procedure. This is typically achieved through the exponential

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or Cayley parametrization of unitary transformations or through simple Jacobi rotations.  

Due to the imposed orthogonality condition, orthogonal LMOs exhibit small nonzero values even far away from the localization center. These orthogonalization tails can complicate the interpretation of chemically relevant electronic-structure information and make its transferability from one system to another more difficult. More importantly, the tails can reduce orbital locality making orbital-based local correlation methods less computationally efficient. To mitigate the undesirable orthogonality effects, metric-preserving unitary transformation has been applied to non-orthogonal orbitals.  

Furthermore, it has been proposed to replace unitary transformation with more general variable-metric nonsingular transformations. This generalization lifts the orthogonality constraint in the localization procedure and increases the number of degrees of freedom available to LMOs. It has been found that non-orthogonal localized molecular orbitals (NLMOs) are indeed about 10–30% more localized than OLMOs if measured by the value of the Boys–Foster function.  

Substantial recent efforts have been made to develop reliable algorithms to construct NLMOs. Despite noticeable progress the existing methods produce NLMOs that are either still fairly similar to OLMOs or lead to the linear dependence between the orbitals. To overcome the linear dependence problem, Yang and co-workers have developed a localization algorithms to construct NLMOs. Despite noticeable deviation from the orthogonality for the unphysical states with linearly dependent occupied orbitals, the allowed one-electron states of the orbital (see below).  

If the NLMOs are normalized, the determinant of \( \sigma \) varies from 1 for orthogonal NLMOs to 0 for linearly dependent NLMOs. The penalty function—the key ingredient of the proposed method—varies from 0 to \( +\infty \) for these two extreme cases, making the linearly dependent state inaccessible in the localization procedure with finite penalty strength \( c_p \). A normalization constraint can be imposed on NLMOs if their coefficients are expressed in terms of independent optimization parameters denoted with lowercase \( a \)

\[
\sigma_{ij} = \langle k|i \rangle = A'_i \sigma^{0}_{ij} A'_j
\]

where the \( a \)-dependent normalization coefficient \( N_j \) is defined for brevity. It should be noted that the normalization requirement does not reduce the flexibility of the localization procedure and can be removed altogether if the penalty function is replaced with its more general version

\[
\Omega_i^N(A) = \Omega_p(A) + \ln \det(\text{diag}(\sigma(A)))
\]

with \( A \) now being independent optimization parameters. It is worth mentioning that the determinant of the NLMO overlap is equal to the square of the volume of the multidimensional parallelepiped spanned by the NLMO vectors, defined by matrix \( A \).

The inclusion of the penalty term converts the localization procedure into an unconstrained, straightforward optimization problem. Additionally, adjusting the strength of the penalty \( c_p \) enables one to achieve the right balance between the non-orthogonality and the locality of the orbitals (see below).

Penalty Strength. If the penalty strength \( c_p \) is extremely large, \( \Omega_i^N \) is negligible compared to the penalty term and the minimization of \( \Omega \) is numerically equivalent to a trivial orbital orthogonalization. In the opposite case of extremely small \( c_p \), the minimization of \( \Omega \) may result in linear dependence between NLMOs reported earlier.  

As we show below, there is a wide range of \( c_p \) values between the two extremes that produce NLMOs that are substantially more localized than OLMOs and linearly independent. A simple strategy to find an appropriate penalty strength is to minimize \( \Omega \) with a sufficiently large initial \( c_p \) value and then gradually decrease \( c_p \) until the determinant of the overlap of the optimal NLMOs drops below a desired threshold \( D_{\text{map}} \in (0, 1] \). The initial value of \( c_p \) should be chosen to balance approximately the localization and penalty components of \( \Omega \). Thus, a reasonable

\[
[1]
\]
initial value of $c_p$ can be estimated by assuming that the reduction in $\Omega$ upon the minimization of $\Omega$ has the same order of magnitude as the change in the penalty $c_p$:  

$$c_p^{\text{init}} \approx \frac{\Omega_1(I) - \Omega_1(A^*)}{\Omega_1(A^*) - \Omega_1(I)} = \beta^*_p \Omega_1(I)$$  

where $A^*$ denotes the (yet unknown) solution to the minimization problem,  

$$\beta^*_p \equiv \frac{\Omega_1(I) - \Omega_1(A^*)}{\Omega_1(I)} \in [0, 1]$$  

is the (positive) expected relative reduction in the localization function, and  

$$\beta^*_p \equiv \ln \frac{\det(\sigma(I))}{\det(\sigma(A^*))} \approx \ln \frac{\det(\sigma(I))}{D_{\text{tar}}} \equiv \beta_p > 0$$  

is the logarithm of the ratio of the initial and final determinants. The importance of eqs 6−8 is that they allow one to estimate the initial value of $c_p$ as a product of $\Omega(I)$, which can be easily calculated in the beginning of the optimization procedure, and a dimensionless constant $\alpha$:  

$$c_p^{\text{init}} = \frac{\beta^*_p}{\beta_p} \Omega_1(I) \equiv \alpha \Omega_1(I)$$  

Equation 9 makes clear that the penalty component is an extensive function of a system with the units that are consistent with the localization component. Although the optimal dimensionless parameter $\beta_p^*$ is not known a priori, its magnitude can be easily estimated to obtain a sufficiently large initial guess for $c_p$. For example, an optimization of canonical orbitals $\det(\sigma(A^*)) = \Omega_{\text{tar}} \approx 0.1$ can be initialized by adopting the maximum possible value of $\beta_p^* = 1$, giving $\alpha = \ln^{-1} 10$.

The procedure for tuning $c_p$ is shown as the outer loop of the optimization algorithm in Figure 1. Its only required input is $D_{\text{tar}}$. It is worth mentioning that the algorithm can be modified to treat the penalty strength as a Lagrange multiplier that imposes the $\Omega(I) = D_{\text{tar}}$ constraint rigorously.

Implementation. In this work, we adopted the localization function proposed by Resta$^{31,32}$ and generalized by Berghold et al.$^{34}$ to three dimensions and simulation cells of general shape and symmetry:

$$\Omega_1(A) = -\sum_K \sum_i \omega_K |z_i^K|^2,$$

$$z_i^K = A_i^K B_{\text{wCA}} K_i$$

\[B_{\text{wCA}} K_i = \langle \psi_i | \mathbf{r} | \psi_i \rangle \]

where $\hat{r}$ is the position operator in three dimensions and $\omega_K$ and $G_K$ are suitable sets of weights and reciprocal lattice vectors, respectively, labeled by index $K$. We chose to write the summation over $K$ explicitly because $K$ is not an orbital index. The function in eq 10 can be used for both gas-phase and periodic systems. In the former case, the function is equivalent to the Boys–Foster localization. In the latter case, its applicability is limited to the electronic states described within the $\Gamma$-point approximation. We also considered the Pipek–Mezey localization function$^{2,25}$ that has the advantage of preserving the separation of $\sigma$ and $\pi$ bonds and is commonly employed for molecular system

**Algorithm 1 Conjugate gradient minimization of $\Omega$**

1. Input $c_{\text{CG}}$ > Localization convergence threshold
2. Input $D_{\text{tar}}$ > Minimum allowed NLMO determinant
3. Input $T_0$ > Initial basis set coefficients for $|i\rangle$
4. Input $S$ > Basis set overlap
5. Input $L^K$ > Basis set representation of the localization operator
6. $\sigma = T_0 S T_0$ > Initial orbital overlap
7. $B^K = T_0 L^K S T_0$ > Initial localization matrix, Eq. (10)
8. $a \leftarrow I$ > Initial guess on variational parameters
9. StopOuter $\leftarrow$ False > Flag to exit the outer loop
10. $c_{\text{Outer}} = 0$ > Iteration counter
11. repeat
12. $c_{\text{Outer}}$ $\leftarrow$ $c_{\text{Outer}} + 1$
13. StopCG $\leftarrow$ False > Flag to exit the CG loop
14. $c_{\text{CG}} = 0$ > Iteration counter
15. repeat
16. $c_{\text{CG}}$ $\leftarrow$ $c_{\text{CG}} + 1$
17. $A \leftarrow \text{diagonal}[\alpha_{\text{CA}}(\sigma_{\alpha})]^{-\frac{1}{2}}$ > Update NLMOs
18. $\sigma \leftarrow A^T \sigma A$ > Update overlap
19. Det $\leftarrow$ determinant($\sigma$) > Determinant
20. $\Omega_p \leftarrow -\ln[\text{Det}]$ > Orthogonlization function
21. $P \leftarrow$ Eq. (15) and (13) > Orthogonalization gradient
22. $\Omega_L \leftarrow$ Eq. (10) > Localization function
23. $L \leftarrow$ Eq. (14) and (13) > Localization gradient
24. if $c_{\text{Outer}} = 1$ and $c_{\text{CG}} = 1$ then
25. $c_p \leftarrow \Omega_1(I)[\ln(D/\text{Det}(D_{\text{tar}}))]^{-1}$ > Initial strength
26. end if
27. $\Omega \leftarrow \Omega_p + c_p \Omega_L$ > Save old gradient
28. if $c_{\text{CG}} > 1$ then
29. $\Gamma \leftarrow G$ > Save old direction
30. end if
31. $G \leftarrow L + c_p P$ > Initial direction
32. if $|G|_{\text{max}} < c_{\text{CG}}$ then
33. StopCG $\leftarrow$ True
34. end if
35. if not StopCG then
36. $O \leftarrow D$ > Line search
37. end if
38. $D \leftarrow -G$ > Search direction
39. if $c_{\text{CG}} > 1$ then
40. $\beta \leftarrow \text{Tr}(G^\dagger D)/\text{Tr}(G^\dagger O)$ > Reduce $c_p$ by factor $r \in (0, 1)$
41. end if
42. if $\alpha \leftarrow \text{argmin}_\Omega (\alpha + \alpha D)$ > Update variational DOFs
43. end if
44. until StopCG
45. if Det $\leq D_{\text{tar}}$ or $c_{\text{Outer}} > N_{\text{Max}}^{\text{Outer}}$ then
46. StopOuter $\leftarrow$ True
47. end if
48. if $c_{\text{Outer}} > N_{\text{Max}}^{\text{Outer}}$ then
49. end if
50. until StopOuter
51. return $T \leftarrow T_0 A$ > Return NLMOs coefficients

**Figure 1. Algorithm for the optimization of NLMOs.**
where \( z_i^k \) is the (real) contribution of orbital \( i \) to the Mulliken charge of atom \( K \) and \( \langle \phi_i^H \rangle \) and \( \langle \phi_i^L \rangle \) are atom-centered covariant and contravariant basis set functions.\(^33,34\) The summation over \( \mu \) is written explicitly to emphasize that it is restricted to the basis functions centered on atom \( K \).

The unconstrained minimization of function \( \Omega \) with fixed \( c_p \) can be carried out with a variety of algorithms. In this work, we used a simple conjugate gradient algorithm summarized in Figure 1. The gradient \( G_k^l \equiv \frac{\partial \Omega}{\partial a_j^l} \) required in the algorithm is a sum of the localization \( L_k^l \equiv \frac{\partial z_k^l}{\partial a_j^l} \) and penalty \( P_k^l \equiv \frac{\partial z_k^l}{\partial \xi_j^l} \) components:

\[
G_k^l \equiv L_k^l + c_P P_k^l
\]

These components can be readily expressed in terms of the derivatives with respect to the transformation coefficients \( \tilde{X}_k^l \equiv \frac{\partial z_k^l}{\partial \xi_j^l} \), where \( X \) is either \( L \) or \( P \):

\[
X_k^l = \tilde{X}_k^l \frac{\partial A_i^l}{\partial a_j^l} = [\tilde{X}_k^l - (\sigma_0^0 A_i^l)(A_i^l \tilde{X}_k^l)]N_j
\]

\[
L_k^l = -\sum_k 4\sigma_0^0 [\text{Re}(B_{km}^K)A_i^l \text{Re}(z_i^K) + \text{Im}(B_{km}^K)A_i^l \text{Im}(z_i^K)]
\]

\[
P_k^l = -2\sigma_0^0 A_m^l \sigma^\mu
\]

If the gradient in eq 14 is computed for the Pipek–Mezey localization function, weights \( \omega_k \) are equal to one and the imaginary part of \( z_i^k \) is equal to zero.

The logarithm of the determinant of the symmetric positive definite overlap matrix \( \sigma \) is computed using the trace of the matrix logarithm via Mercator series:

\[
\ln \det(\sigma) = \ln[\det(s)] \det(I + X) \det(s)]
\]

\[
\ln \det(I + X) = \text{Tr} \ln[I + X],
\]

\[
\ln[I + X] = X - \frac{1}{2}X^2 + \frac{1}{3}X^3 - \frac{1}{4}X^4 + ...
\]

where \( s = [\text{diag}(\sigma)]^{1/2} \). The series converges only if \( \|X\|_F < 1 \). If it is not the case, the square root of \( I + X \) is computed recursively until the norm requirement is satisfied. The advantage of this algorithm is that it relies exclusively on matrix–matrix multiplication and can be readily implemented in any matrix library. Its computational cost grows cubically with the number of orbitals for dense matrices and linearly for sparse overlap matrices of localized orbitals.

The localization procedure was implemented in the CP2K software package.\(^48\) The DBCSR library\(^49\) that handles sparse matrices efficiently on massively parallel computing platforms is utilized to enable orbital localization in large systems.

**Computational Details.** To test the localization procedure, we constructed NLMOs for several systems ranging from a simple water molecule to complex molecules with nontrivial bonding patterns and to large periodic systems. For all systems, the initial CMOs were obtained using the conventional diagonalization-based SCF procedure implemented in the electronic-structure module of CP2K. The Becke–Lee–Yang–Parr generalized gradient approximation\(^50,51\) was used as the exchange–correlation functional. Goedecker–Teter–Hutter pseudopotentials\(^52\) were used together with a triple-\( \zeta \) atom-centered Gaussian basis set with two sets of polarization functions for all atoms. The energy cutoff was set at 600 Ry to define the auxiliary plane-wave basis set in the construction of the effective Hamiltonian. The integration over the Brillouin zone was performed using the \( \Gamma \)-point approximation.

### RESULTS AND DISCUSSION

**Compromise between Locality and Orthogonality.** For all test systems, the conjugate gradient localization procedure in
The initial value of $D_{\text{tar}} = 10^{-1}$ in all tests. The initial value of $\alpha = \ln^{-1} 10$ was set according to eq 9. The value of $\alpha$ was decreased by a factor of 2 in the outer loop of the algorithm (Figure 1) until the overlap determinant fell below $D_{\text{tar}}$ or until the optimal $\Omega_i$ stopped changing with $c_\Omega$ appreciably (see water, diborane, and heptane examples in Figure 2).

Since the determinant of the overlap is proportional to the square of the volume of the parallelepiped spanned by the NLMO vectors, $D_{\text{tar}} = 10^{-1}$ corresponds to the volume of $\det(A) \approx 0.32$, which is large enough to produce distinct NLMOs.

Figure 2 demonstrates how the penalty strength affects the optimal orbital localization and the determinant of the orbital overlap. In all tests, the initial penalty strength is sufficiently large to produce almost perfectly orthogonal localized orbitals. At the same time it is too large to yield more localized non-orthogonal localized orbitals after just several steps of $c_\Omega$ adjustment.

Figure 2 shows that within a large range of values spanning $3 \sim 6$ orders of magnitude $c_\Omega$ serves as an adjustable parameter that can be tuned to achieve a desirable locality–orthogonality compromise. Thus, the flexibility of the unconstrained localization method presented here allows one to combine the strengths of the existing localization methods that produce either orthogonal orbitals or NLMOs with fixed localization centers. It is also important to emphasize that the localization procedure is unconstrained, does not require complicated parametrization of unitary matrices, and relies on a simple easy-to-implement conjugate gradient optimization algorithm.

NLMOs More Localized than OLMOs. Figure 2 reveals the expected trend: the orbitals become more localized as they are allowed to be less orthogonal. The relative reduction in the localization is quantified by $\Delta_{X/Y} \equiv \frac{\Omega_i(Y) - \Omega_i(X)}{\Omega_i(Y)} \times 100\%$, where $X$ and $Y$ can refer to CMOs, OLMOs (obtained with the conventional unitary transformations), or NLMOs. Table 1 compares the relative reduction as measured by the Berghold function for OLMO/CMO, NLMO/CMO, and NLMO/OLMO pairs. Although NLMOs are constructed with $D_{\text{tar}}$ set to $10^{-1}$, most final values of the NLMO overlap determinants (last column in Table 1) are somewhat lower than $D_{\text{tar}}$ because the last outer-loop iteration brings $\det(\sigma)$ below $D_{\text{tar}}$.

The relative reduction in localization between OLMOs and CMOs ranges from 22% to 98% and reaches high values for extended systems (e.g., icosane) where the localization has the ability to reduce the spread significantly. The average relative reduction for the data set considered here is 70%. The NLMOs are even more localized than OLMOs. The relative reduction in localization between NLMOs and OLMOs ranges from 6% to 30% with the data set average of 18%. This additional reduction in the orbital spread can lead to a substantial reduction in the number of significant excitation amplitudes in local electron-correlation methods and to noticeable computational savings.

The relative reduction in localization between OLMOs and NLMOs is similar to that obtained with the algorithms that fix NLMO localization centers.\(^{42,43}\) Since the NLMO centers were previously fixed at the position of OLMO centers, this implies that the locations of the centers of NLMOs and OLMOs are very similar. It also suggests that the NLMOs obtained with $D_{\text{tar}} = 10^{-1}$ represent the electronic structure of molecules reliably and also serves as an additional verification of the previously employed fixed-center procedures.

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**Table I. Relative Reduction in the Localization Function and the Final Determinant of the NLMO Overlap**

| molecules                  | $\Delta_{\text{OLMO/CMO}}$ | $\Delta_{\text{NLMO/CMO}}$ | $\Delta_{\text{NLMO/OLMO}}$ | $\det(\sigma)$ |
|----------------------------|-----------------------------|-----------------------------|-----------------------------|----------------|
| H$_2$O                     | 22                          | 36                          | 18                          | 0.100          |
| CO$_2$                     | 65                          | 76                          | 30                          | 0.025          |
| diborane (B$_2$H$_6$)      | 62                          | 64                          | 6.2                         | 0.745          |
| borazine (B$_2$N$_6$H$_6$) | 73                          | 78                          | 20                          | 0.026          |
| carborane (C$_2$B$_6$H$_12$)| 72                          | 76                          | 17                          | 0.085          |
| propene (C$_3$H$_6$)       | 61                          | 67                          | 14                          | 0.042          |
| 1-butene (C$_4$H$_6$)      | 62                          | 70                          | 19                          | 0.063          |
| benzene (C$_6$H$_6$)       | 69                          | 78                          | 28                          | 0.041          |
| heptane (C$_7$H$_8$)       | 89                          | 90                          | 12                          | 0.122          |
| icosane (C$_{20}$H$_{42}$) | 98                          | 98                          | 11                          | 0.053          |
| decacyclene (C$_{72}$H$_{24}$)| 94                          | 95                          | 16                          | 0.042          |
| graphene                   | 77                          | 82                          | 21                          | 0.025          |
| average                    | 70                          | 76                          | 18                          | 0.114          |

Figure 3 shows that the NLMOs obtained with $D_{\text{tar}} = 10^{-1}$ represent the electronic structure of molecules reliably and also serves as an additional verification of the previously employed fixed-center procedures.
electron pairs. Although NLMOs are more localized and extend only over two carbon atoms, they tend to take the shape of a mixture between $\sigma$ and $\pi$ bonds producing the so-called $\tau$ orbitals. To prevent the $\sigma-\pi$ mixing, the Berghold localization function was replaced with the Pipek–Mezey function.

The OLMOs and NLMOs obtained with the Pipek–Mezey and Berghold localization schemes were compared for benzenel and allyl alcohol (Figure 6). For OLMOs, the Pipek–Mezey scheme preserves the separation between the $\sigma$ and $\pi$ bonds. Upon a visual inspection of NLMOs of these systems, Pipek–Mezey orbitals appear to be more localized than those obtained with the Berghold (i.e., Boys–Foster) scheme. A quantitative comparison of the locality of Pipek–Mezey and Berghold LMOs is difficult because there is no universal function that measures orbital locality. If the Pipek–Mezey function is chosen as a common measure to compare the locality of LMOs, then Pipek–Mezey NLMOs appear more local because they minimize the common measure by definition (Figure 7, lower panel). If the common measure is chosen to be the Berghold spread, then Berghold NLMOs appear more local for the same reason (Figure 7, upper panel).

It is important to note that as the determinant of the NLMO overlap decreases the $\sigma-\pi$ separation of the Pipek–Mezey scheme is not maintained and a pair of $\sigma$ and $\pi$ bonds tend to mix generating a pair of $\tau$ and $\tau'$ NLMOs (Figure 6). It has been shown that, in the original Pipek–Mezey localization scheme designed for OLMOs, $\tau$ and $\tau'$ orbitals cannot be more localized than $\sigma$ and $\pi$ orbitals:

$$\Omega_{\text{PM}}^{\sigma}(\sigma) + \Omega_{\text{PM}}^{\pi}(\pi) \leq \Omega_{\text{PM}}^{\tau}(\tau) + \Omega_{\text{PM}}^{\tau'}(\tau')$$

Here we used a simple two-orbital system as an example to demonstrate that, in the case of NLMOs, the Pipek–Mezey localization function can generate $\tau$ and $\tau'$ as the most localized solution. We consider two atoms A and B, each with $p_x$ atomic orbitals, separated along the x axis as shown in Figure 8A. The canonical bonding $\langle \sigma | \sigma \rangle$ orbital is represented by the positive linear combination of two $p_x$ atomic orbitals. Mixing the occupied $\sigma$ and $\sigma^*$ orbitals produces $\tau$ and $\tau'$ orbitals:

$$\begin{align*}
|\tau \rangle &= |\sigma \rangle \cos(\Theta) + |\pi \rangle \sin(\Theta) \\
|\tau'^* \rangle &= -|\sigma \rangle \sin(\Theta) + |\pi \rangle \cos(\Theta)
\end{align*}$$

In the general case of NLMOs, there are two mixing angles $\Theta$ and $\Phi$ that can be varied independently to minimize $\Omega_{\text{PM}}^{\tau \tau'}$. OLMOs are recovered when $\Theta = \Phi$. Figure 8B shows the dependence of the Pipek–Mezey localization function on $\Theta$ and $\Phi$. The red diagonal line corresponds to all possible OLMOs. The metric-preserving yellow line describes the NLMOs with $\det(\sigma) = 10^{-2}$. As shown in the work of Pipek and Mezey, the $\sigma$ and $\pi$ orbitals ($\Theta = \Phi = 0$) minimize the localization function along the diagonal line. But as the orbitals are allowed to be less orthogonal, the most localized solution $\Theta = \Phi = \pi/2$ corresponds to $\tau$ and $\tau'$. This simple example shows that, generally speaking, $\sigma-\pi$ separation cannot be expected for NLMOs even if they are constructed with the Pipek–Mezey method.

**CONCLUSIONS**

In this work, we proposed a new approach to construct localized orthogonal and non-orthogonal one-electron orbitals. In this approach, the catastrophic linear dependence of the orbitals is prevented by augmenting the localization function with a simple...
single-value penalty that measures the degree of orbital nonorthogonality and thus allows one to avoid nearly dependent states in the localization procedure. The proposed penalty function enables a more flexible approach to orbital localization as it allows one to replace traditional metric-preserving unitary transformations of the orbitals with more general variable-metric nonsingular transformations. The approach is also conceptually simpler because a complicated parametrization of unitary transformations is obviated, even in the case of OLMOs, allowing one to optimize orbital mixing coefficients directly using simple unconstrained minimization algorithms.

The new approach is easy to implement as was demonstrated for the Berghold and Pipek–Mezey localization functions. Numerous tests were performed for gas-phase and periodic systems. For gas-phase molecules, the Berghold scheme is
The tests show that orbital localization is robust when implemented with a simple conjugate gradient algorithm. The procedure generates NLMOs without a priori knowledge of bonding patterns in the system. An additional black-box algorithm is proposed to tune the penalty strength and produce the desired balance between the orthogonality and locality of NLMOs. The desired balance is specified as the minimum allowed determinant of the NLMO overlap matrix—an intuitively clear parameter in the (0,1] range. We found that NLMOs with the minimum allowed determinant of the order of $10^{-1}$ correctly recover bonding patterns in a variety of molecules and materials, including large systems with nontrivial bonding. NLMOs are approximately 18% more localized than OLMOs and have reduced tails. This observation is consistent with previous results obtained for the NLMOs with the localization centers fixed at the OLMO positions.\textsuperscript{4,43} It serves as an additional verification of the previously employed procedures and implies that the NLMOs representation of the electronic structure of molecules is reliable.

To our surprise, the Pipek–Mezey localization, which has been a reliable method to separate orthogonal $\sigma$ and $\pi$ orbitals in locally planar systems with double bonds, tends to mix these orbitals when they are allowed to become strongly non-orthogonal. The origins of this effect was explained using a simple two-orbital system as an example.

The broader significance of this work is in the new continuous easy-to-compute non-orthogonality measure that can be adopted by a variety of electronic-structure theories that benefit from non-orthogonal representation of wave functions.

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\section{Notes}

The authors declare no competing financial interest.

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