

Properties of the simplest localized molecular orbitals: the P-LMOs

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Columns of the LCAO density matrix, $\mathbf{P}$, obtained in a standard Hartree-Fock or Kohn-Sham calculation, can be interpreted as coefficients of occupied localized molecular orbitals (LMOs). Requiring no extra calculations once $\mathbf{P}$ is available, they constitute the simplest possible set of occupied LMOs. They are nonorthogonal, moreover redundant, and are related to the usual projected atomic orbitals which emerge as the columns of matrix $\mathbf{PS}$, where $\mathbf{S}$ is the overlap matrix of atomic orbitals. Both P-LMOs and PS-LMOs may serve as molecular orbitals even for procedures that determine $\mathbf{P}$ directly, i.e., avoiding the construction of molecular orbitals. To enhance localization, the LMOs resulting from the square root of $\mathbf{P}$ are also investigated. Properties of P-LMOs and $\mathbf{P}^{1/2}$ -LMOs are discussed and they are compared to PS-LMOs and to other well-known types of localized orbitals.

I. INTRODUCTION

Localized molecular orbitals (LMOs) are of interest both for their computational and interpretative advantages. While approximate LMOs may also be useful, we shall discuss here only those that span the exact occupied subspace in a Hartree-Fock (HF) or Kohn-Sham calculation.

Classification of LMOs can be done along various points of view. *A posteriori* LMOs are obtained by some techniques after the HF equations have been solved, while *a priori* LMOs result from modifying the HF procedure to yield LMOs directly, instead of determining first the canonical MOs (CMOs). Though several ideas for the latter have been proposed,¹⁻⁵ this field is still in the research stage, while the former constructions are standard and widely used.

A posteriori LMOs can be obtained from CMOs by a procedure that relies on a localization criterion. The latter can be external⁶⁻⁸ or internal, applying some localization functional which is made extremal iteratively⁹⁻¹⁵. These iterations, depending on the size of the problem and the nature of the functional, can be demanding computationally. Therefore, there is a strong interest in search for noniterative LMOs.

The simplest noniterative LMOs which have widely been used emerge from projecting atomic orbitals (AOs, denoted by χ) into the occupied (or virtual) subspace as

$$|\phi_\mu^{PS}\rangle = \hat{P}|\chi_\mu\rangle, \quad (1)$$

where for occupieds

$$\hat{P} = \sum_i^{\text{occ}} |\psi_i\rangle\langle\psi_i|, \quad (2)$$

where ψ_i are some orthonormal MOs that span the occupied subspace, say the CMOs. (An analogous projector can be used to generate virtuals.) The superscript **PS** in Eq.(1) indicates that the LCAO coefficients of LMOs ϕ_μ^{PS} are, in fact, the columns of matrix **PS**, as readily seen by substituting the LCAO expansion of CMOs with coefficients $C_{\lambda i}$ into (2):

$$\begin{aligned} |\phi_\mu^{PS}\rangle &= \sum_i^{\text{occ}} |\psi_i\rangle\langle\psi_i|\chi_\mu\rangle \\ &= \sum_{\lambda\sigma} \sum_i^{\text{occ}} C_{\lambda i} C_{\sigma i}^* |\chi_\lambda\rangle\langle\chi_\sigma|\chi_\mu\rangle \\ &= \sum_{\lambda} (PS)_{\lambda\mu} |\chi_\lambda\rangle, \end{aligned} \quad (3)$$

with the AO overlap matrix $S_{\sigma\mu} = \langle \chi_\sigma | \chi_\mu \rangle$ and the LCAO density matrix

$$P_{\lambda\sigma} = \sum_i^{occ} C_{\lambda i} C_{\sigma i}^*.$$

The localized nature of ϕ_μ^{PS} -s stems from the fact that they are projected AOs. The set $\{|\phi_\mu^{PS}\rangle\}_{\mu=1}^M$ is nonorthogonal and redundant, as their number is the no. of basis functions, M , not that of the occupied orbitals, N_{occ} . This redundancy is handled usually by using only a subset of them, e.g. selecting a limited number of AOs, or by choosing the N_{occ} LMOs having the largest norms.^{16–20} Another solution was proposed by Fuemmeler et al.²¹, who applied a QR factorization of matrix **PS**. Virtual analogues of PS-LMOs can also be formed easily by using the hole density matrix, and they find extensive use in current applications.²²

II. P-LMOS

Nonorthogonal, redundant LMOs can also be defined considering simply the columns of matrix **P** (instead of **PS**) as LCAO coefficients:

$$|\phi_\mu^P\rangle = \sum_\nu P_{\nu\mu} |\chi_\nu\rangle. \quad (4)$$

We shall refer to this set as P -LMOs. They are rarely applied in spite of their simplicity. A notable exception is the method of Aquilante et al.²³, who derived orthogonal LMOs from (4) by Cholesky-decomposing matrix **P**. An advantage of this procedure is that one obtains orthonormal LMOs at a low cost. Since Cholesky-decomposition is related to Schmidt orthogonalization,²⁴ the Cholesky-decomposed **P** may yield LMOs with broken spatial symmetry. P -LMOs resulting from the subset of AOs invariant under symmetry transformations do not show this problem, they, however, represent a redundant set.

Columns of the density matrix are used as LMOs in Refs.^{21,25} These works first represent the density matrix (and the canonical orbitals) numerically on a grid. This is appropriate for extended systems or if plane-wave basis sets are used, but less natural for local Gaussian AO basis sets. In the latter case, when applying the algorithm for molecules²¹, Fuemmeler et. al. either orthogonalize the AOs or deal with matrix **PS** rather than with **P**.

The fact that the P -LMOs lie in the occupied subspace can be demonstrated by expanding matrix **P** through the coefficients of CMOs $\psi_i = \sum_\nu C_{\nu i} \chi_\nu$:

$$|\phi_\mu^P\rangle = \sum_i^{occ} \sum_\nu C_{\nu i} C_{\mu i}^* |\chi_\nu\rangle = \sum_i^{occ} C_{\mu i}^* |\psi_i\rangle. \quad (5)$$

That is, the P -LMOs are linear transformations of the occupied CMOs, with the transformation matrix constructed from the CMO coefficients. It follows therefore that

$$\hat{P}|\phi_\mu^P\rangle = |\phi_\mu^P\rangle. \quad (6)$$

The reverse relation, that is expressing CMO ψ_k in terms of P-LMOs, can be obtained from (5) by multiplying it first with $\mathbf{S}$ and then with $\mathbf{C}$ from the right and using the CMO normalization condition $\mathbf{C}^\dagger \mathbf{S} \mathbf{C} = \mathbf{I}$ to yield

$$|\psi_k\rangle = \sum_\mu (\mathbf{S}\mathbf{C})_{\mu k} |\phi_\mu^P\rangle. \quad (7)$$

Note that expansion (7) is not unique, since the set of P-LMOs is linearly dependent in general.

The sparsity of matrix $\mathbf{P}$ ensures the localized nature of ϕ_μ^P -s. In more detail, let us imagine orthonormal MOs characterized by coefficients $C_{\mu i}^L$, which are most localized in some sense. They also determine the unitary-invariant matrix $\mathbf{P}$ as

$$P_{\lambda\sigma} = \sum_i^{occ} C_{\lambda i}^L (C_{\sigma i}^L)^*.$$

This means that in order to have a nonzero matrix element $P_{\lambda\sigma}$, there must exist at least one localized molecular orbital i in the above sum which has nonzero components on both AOs χ_λ and χ_σ . Accordingly, the sparsity of $\mathbf{P}$ depends on the existence of sufficiently localized MOs, whether we have *de facto* determined them or not. The absence of the overlap matrix $\mathbf{S}$ from the definition (4) suggests that P-LMOs are more localized than the projected LMOs ϕ^{PS} . This will be numerically investigated in the following section.

While matrix $\mathbf{P}\mathbf{S}$ is idempotent:

$$\mathbf{P}\mathbf{S}\mathbf{P}\mathbf{S} = \mathbf{P}\mathbf{S} \quad (8)$$

(as it readily follows from the idempotency of the projection operator in Eq.(2)), it is not hermitian: $(\mathbf{P}\mathbf{S})^\dagger = \mathbf{S}\mathbf{P}$). Such a matrix is sometimes called a skew-projector²⁶. Matrix $\mathbf{P}$ has reverse properties: it is hermitian but not idempotent in an overlapping AO basis. This means that repeated transformation by $\mathbf{P}$ does not leave the MOs ϕ_μ^P intact:

$$\sum_\mu P_{\mu\nu} |\phi_\mu^P\rangle \neq |\phi_\nu^P\rangle.$$

Nevertheless, it does not generate any virtual components when transforming occupied MOs. At the same time, it annihilates all virtual components when transforming a set of arbitrary vectors, cf. eq.(5). A non-idempotent matrix (or operator) which transforms within a subspace but wipes any components outside of that subspace could be baptized a *razor*.

The overlap matrix of P-LMOs is easy to obtain as

$$\langle \phi_\mu^P | \phi_\nu^P \rangle = \sum_{\lambda\sigma} P_{\mu\lambda} P_{\sigma\nu} \langle \chi_\lambda | \chi_\sigma \rangle = (\mathbf{PSP})_{\mu\nu} = \mathbf{P}_{\mu\nu}. \quad (9)$$

The last equation emerges from the relation $\mathbf{PSP} = \mathbf{P}$, which results from (8) assuming that the AO overlap matrix $\mathbf{S}$ is positive definite thus it can be inverted. I.e., the overlap matrix of P-LMOs is simply $\mathbf{P}$ whose rank is N_{occ} .

Eq. (9) has the interesting consequence that P-LMOs can be normalized to unity in a cost-less manner:

$$\phi_\mu^{\text{normalized}} = \frac{1}{(P_{\mu\mu})^{1/2}} \sum_\nu P_{\nu\mu} \chi_\nu \quad (10)$$

Redundancy of P-LMOs can be treated in the same manner as it is commonly done for the projected PS-LMOs mentioned in the introduction. In this paper we do not deal with this problem, we merely demonstrate the localized extent of the density-matrix-based LMOs.

III. $\mathbf{P}^{1/2}$ -LMOS

The above-mentioned fact, that repeated application of matrix $\mathbf{P}$ on occupied MO coefficients does not bring out from the occupied space, has some interesting consequences. First, if one insists on having a hermitian matrix which is idempotent, one may apply the McWeeny iterative purification algorithm²⁷ (or a variant thereof):

$$\mathbf{P}' = 3\mathbf{P}^2 - 2\mathbf{P}^3.$$

One should only take care of preserving the rank of $\mathbf{P}$ during the iteration, to get a true projector for the occupied space upon convergence, that is both idempotent and hermitian. We do not explore this direction further, as multiplying by $\mathbf{P}$ repeatedly will certainly gradually delocalize the resulting MOs.

However, one may raise the question what we get if we apply, in a certain sense, a reverse procedure: instead transforming the AOs with $\mathbf{P}$, we do this with its square root:

$$|\phi_\mu^{P^{1/2}}\rangle = \sum_\nu P_{\nu\mu}^{1/2} |\chi_\nu\rangle \quad (11)$$

with a shorthand for the elements of the square root of matrix $\mathbf{P}$. As $\mathbf{P}$ is hermitian and positive semidefinite, matrix $\mathbf{P}^{1/2}$ is well defined and can be uniquely constructed by taking the positive square root of all nonzero eigenvalues of $\mathbf{P}$. (The latter are not 1.0 for overlap effects.) If the LMOs obtained e.g. by $\mathbf{P}^2$ are expected to be less localized than those obtained by $\mathbf{P}$, then one may hope intuitively that the LMOs from (11) are in turn, more localized. This will also be numerically illustrated in the following section.

The $\mathbf{P}^{1/2}$ -LMOs have the special feature that the sum of their square norms equals the number of occupied orbitals N . This can be easily seen by evaluating their overlap matrix

$$\langle \phi_\mu^{P^{1/2}} | \phi_\nu^{P^{1/2}} \rangle = \sum_{\lambda\sigma} P_{\mu\lambda}^{1/2} S_{\lambda\sigma} P_{\sigma\nu}^{1/2},$$

where $\mathbf{S}$ is the basis overlap matrix. The trace of this LMO overlap matrix gives the sum of square norms of the LMOs:

$$\text{Tr} (\mathbf{P}^{1/2} \mathbf{S} \mathbf{P}^{1/2}) = \text{Tr} (\mathbf{PS}) = N.$$

IV. NUMERICAL ILLUSTRATIONS

The model system we consider is a linear chain of 100 H atoms, in two types of geometries. The first is an equidistant chain with $r(\text{HH})=0.74 \text{ \AA}$. The other is an alternating geometry with $r_1(\text{HH})=0.74 \text{ \AA}$ and $r_2(\text{HH})=0.84 \text{ \AA}$. For the latter, more enhanced localizability is expected. The case of equidistant bond lengths will be abbreviated as "metallic", though this is somewhat euphemistic for only 100 sites (the HOMO-LUMO band gap is 0.34736 a.u. for the alternating geometry, and 0.18516 a.u. for the equidistant case). The Huzinaga MINI basis set²⁸ was used. In both cases, two indicators will be monitored: a) the decay of LMO coefficients along the chain, and b) the average size of the LMOs. The size of LMO ϕ_i is defined^{11,29,30} as the distribution (second central moment) of the coordinate operator $\hat{r}$:

$$r_i = \langle \phi_i | \hat{r}^2 | \phi_i \rangle - \langle \phi_i | \hat{r} | \phi_i \rangle^2. \quad (12)$$

Minimizing the sum of these orbital spreads was proven¹¹ to be equivalent with the Foster-Boys localization criterion maximizing orbital centroid distances.

A. P-LMOs vs. PS-LMOs

Figure 1. shows the coefficients of two selected LMOs along the alternating chain of H atoms, one at the very left (a "surface LMO") and another the middle of the chain (a "bulk LMO"). Fig.1.a exhibits the overall picture. It gives the impression that the the bulk LMOs fall off more quickly if obtained from matrix **PS**, while the two kinds of surface LMOs are quite similar. However, zooming into the domain of the tail of LMOs (Fig. 1.b) it is clearly shown that the fall-off of P-LMOs is somewhat faster. (The figure compares only the two bulk LMOs, but the situation for the two surface LMOs is the same.)

The two parts of the figure are not contradictory: since the LMOs are normalized to unity (in metric **S**), if the P-LMOs at around their centroids have larger coefficients in absolute values (Fig.1.a), then they are expected to fall off more quickly to reach the same normalization.

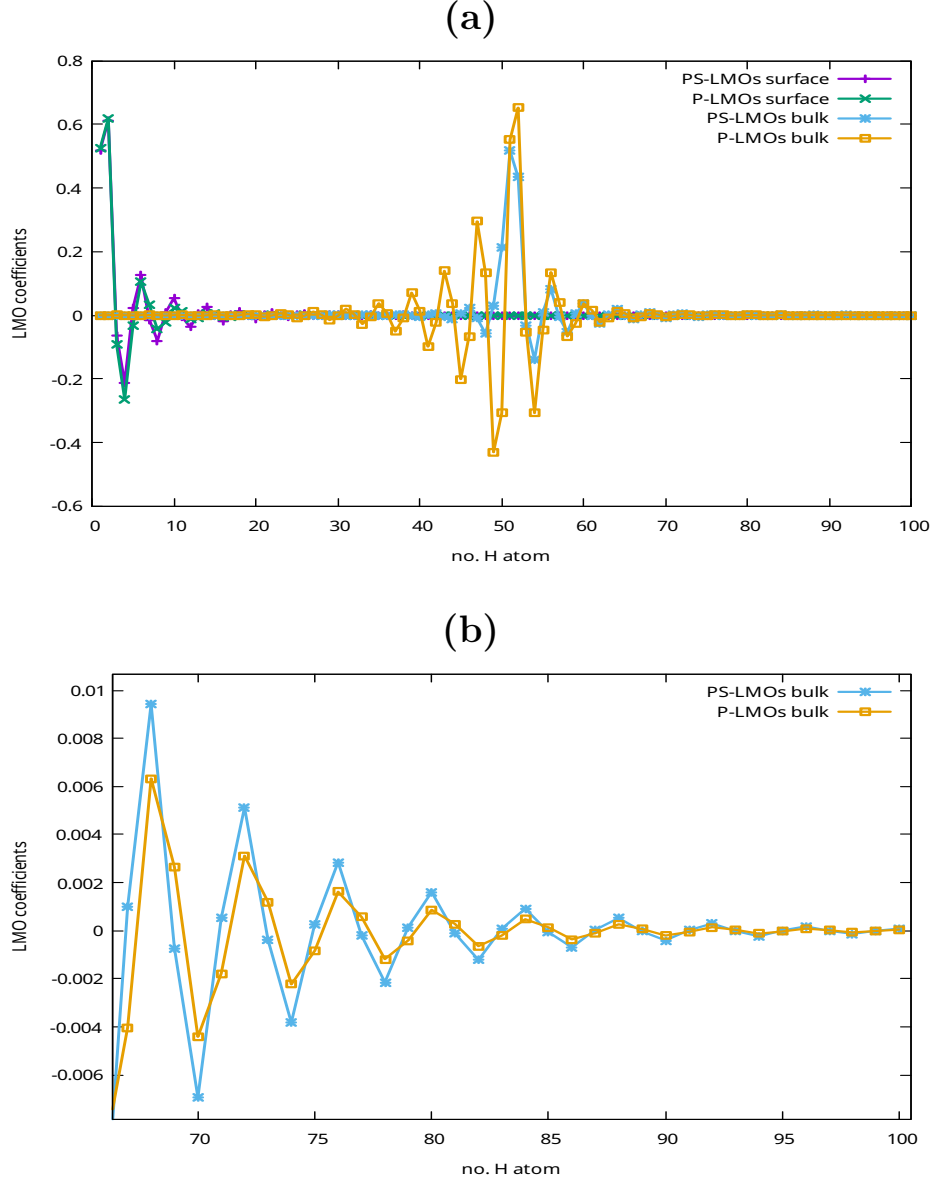
Figure 2. shows the results for the metallic-type chain. Again, Fig.2.a shows the overall picture, while Fig.2.b depicts the asymptotics of LMOs (in this case, the surface ones). It is apparent that the fall-off of both surface- and bulk-LMOs is slower in Fig.2. than it was in Fig.1., which is a consequence of the metallic-like geometry for which the localizability is known to be worse. However, one may see that for this long but finite metallic chain the localizability is still quite good, even if somewhat worse than for the alternating geometry. As to the comparison of P- and PS-LMOs, the latter are slightly more localized both in the surface and bulk cases, but they are rather similar to each other.

To characterize the fall-off of these LMOs more quantitatively, we considered the absolute values of their coefficients (for a surface LMO, see Fig. 3.). The values have been fitted by a simple exponential curve

$$f(x) = A e^{-\zeta x}. \quad (13)$$

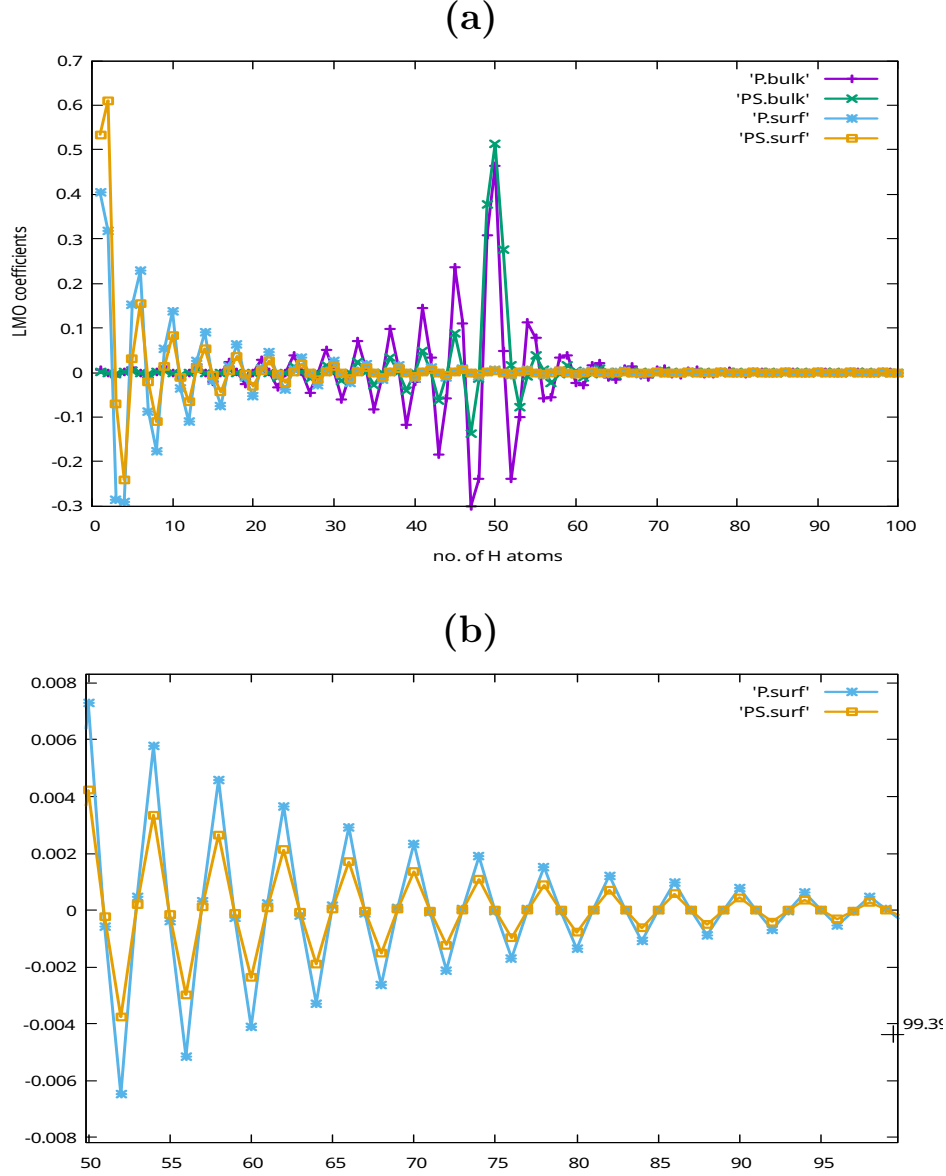
The larger the fitted exponent ζ is, the more localized is the LMO in question. Fig. 3 indicates that tails of LMOs fall off exponentially even for the metallic-like geometry. The fitted exponent for various cases are tabulated in Table I. The data clearly show that the exponents for the alternating geometry are significantly larger (almost double) than for the equidistant case, showing the enhanced localizability for the latter. Difference between the asymptotic exponents of P- and PS-LMOs are almost negligible in both cases, the localizability of PS-LMOs showing tiny little better.

FIG. 1. Comparison of the LCAO coefficients of P- and PS-LMOs in the bulk and on the surface for the alternating chain of 100 H atoms. (a): overall picture, (b): asymptotics



A somewhat different picture emerges when checking the LMO sizes defined by Eq.12. They are also put in Table I. indicating that the sizes of P-LMOs are larger in average. This is due to that they have larger coefficients at around their centroids, while the domain of tails where they fall off faster does not really contribute to their sizes defined by Eq.(12). The PS-LMOs are more compact also in the case of metallic (equidistant) geometry. Note that the sizes are significantly larger in the metallic case, though both the P- and PS-localization works: the LMO sizes are in the order-of-magnitude of an Å, while the length of the full

FIG. 2. Comparison of the LCAO coefficients of P- and PS-LMOs in the bulk and on the surface for the equidistant chain of 100 H atoms. (a): overall picture, (b): asymptotics



chain is 73 (78) Å for the equidistant (alternating) geometries, respectively.

B. P-LMOs vs. standard iterative LMOs

Fig. 4 depicts the bulk LMOs in the "metallic" H_{100} chain obtained from the Edmiston-Ruedenberg procedure and the respective normalized column of the P matrix. While the ER-LMO at the middle of the chain has left-right symmetry, The P-LMO is slightly asymmetric.

FIG. 3. Fall-off of absolute values of P-LMO coefficients for the metallic geometry of the H_{100} chain in the asymptotic region. The wider solid line is a fit to the coefficients with an exponential function for the leftmost surface LMO.

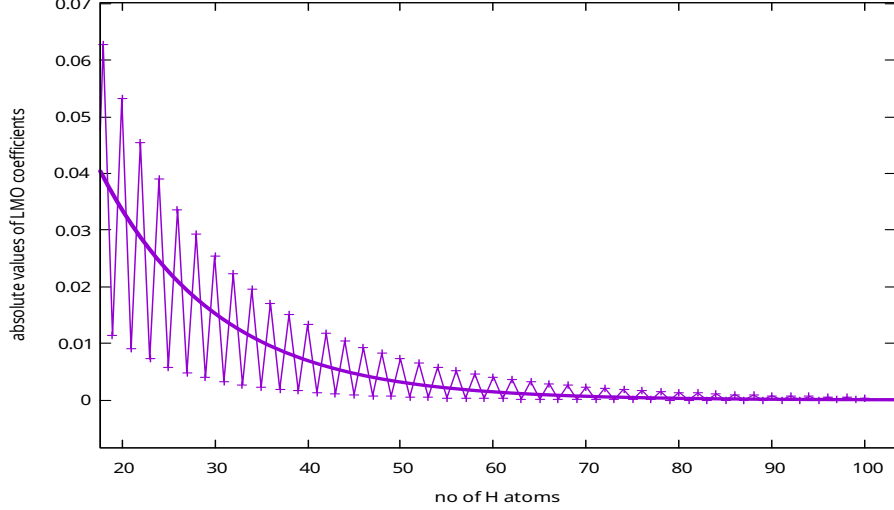


TABLE I. Asymptotic exponents and average sizes of P- and PS-LMOs for the chain of 100 H atoms. The exponents are computed for a surface LMO, fitted for the range of [20:100] atom, and tabulated in arbitrary units.

method of localization	geometry	exponent ζ	LMO size [$\text{\AA}$]
PS-LMOs	alternating	0.1936	1.071
P-LMOs	alternating	0.1930	1.810
PS-LMOs	equidistant	0.0789	1.157
P-LMOs	equidistant	0.0788	2.739

This is a consequence of that the ER procedure localizes the MOs onto bonds, the P-LMOs are atom-centered, and in a chain of even atoms there is a middle bond, but there is no middle atom. This asymmetry is also manifested in the asymptotics: ER LMOs fall off more quickly at the left-side, while P-LMOs are better at the right side.

Surface LMOs behave similarly (see Fig.5). Note the exponential falloff of all LMOs even for the equidistant chain.

The conclusions are slightly different for the case of alternating geometry. Fig. 6 shows the comparison of the leftmost surface ER- and P-LMOs with the inset exhibiting the asymptotics. It seems that P-LMOs fall off more quickly than the ER ones in this example. This

FIG. 4. Comparison of Edmiston-Ruedenberg (ER) and P-LMOs for the equidistant chain of H atoms: bulk LMOs

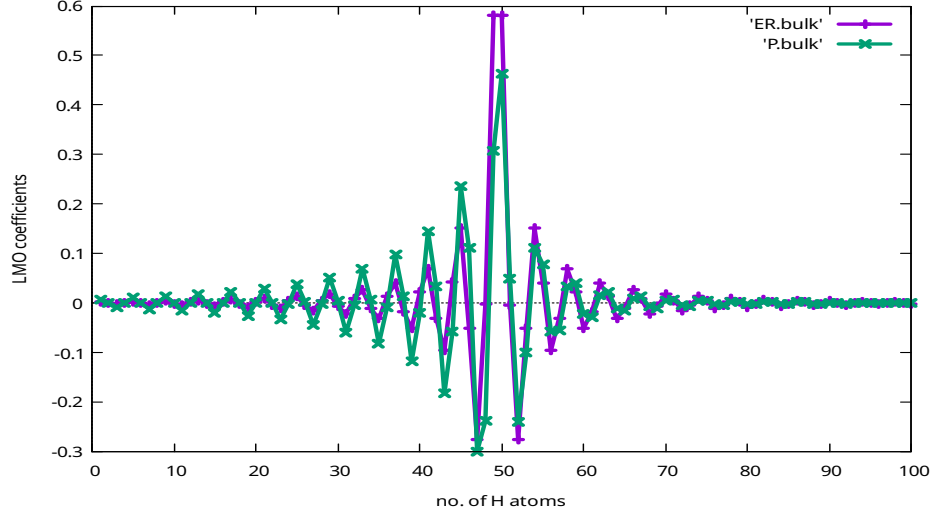
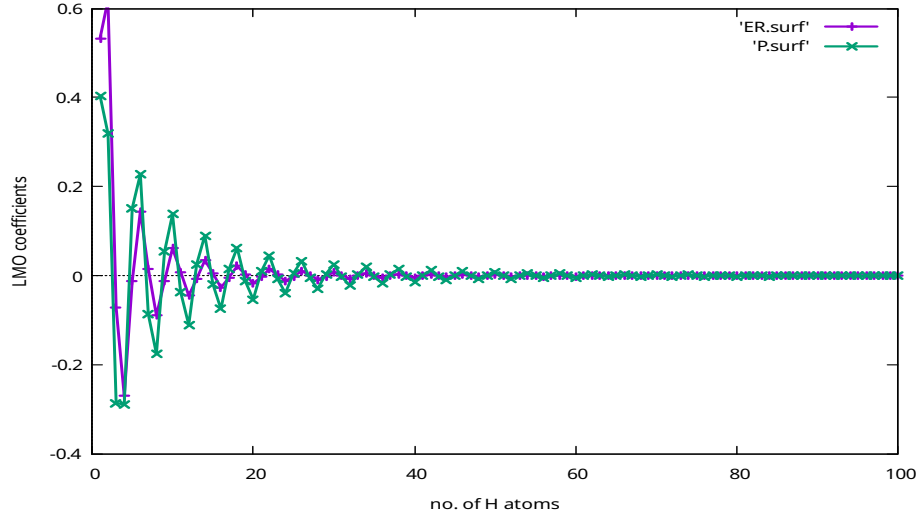


FIG. 5. Comparison of Edmiston-Ruedenberg (ER) and P-LMOs for the equidistant chain of H atoms: surface LMOs



is well reflected by the fitted fall-off exponents of these surface LMOs: 0.166 for Edmiston-Ruedenberg ones and 0.219 for the P-LMOs (the fitted region was between the 5th and 50th H atom).

Boys LMOs and Pipek-Mezey LMOs were also checked for both geometries, but not shown on figures as they practically coincide with the ER-LMOs for this simple model system.

Table II shows the average sizes of LMOs obtained by various iterative localization procedures and by P-LMOs. The sizes are computed according to Eq. (12). The numbers reflect

FIG. 6. Comparison of Edmiston-Ruedenberg (ER) and P-LMOs for the alternating chain of H atoms: surface LMOs

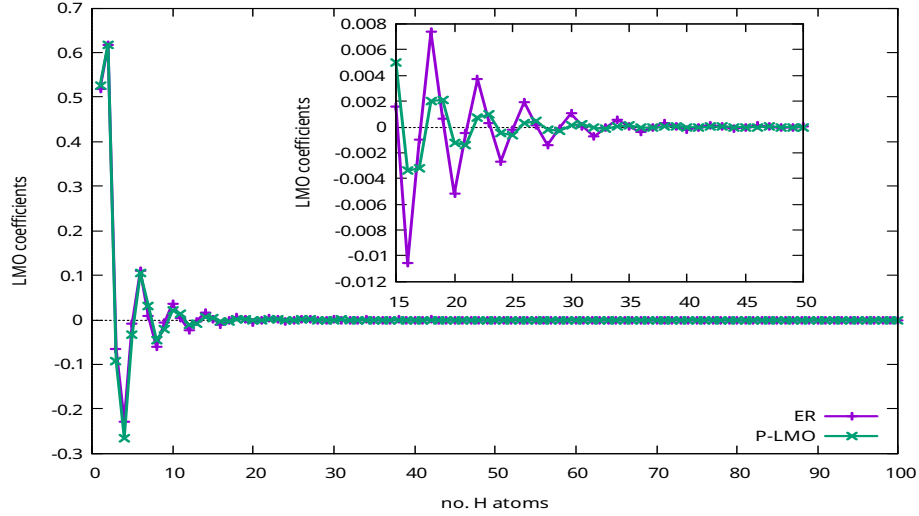


TABLE II. Average sizes of iterative LMOs and P-LMOs [$\text{\AA}$]

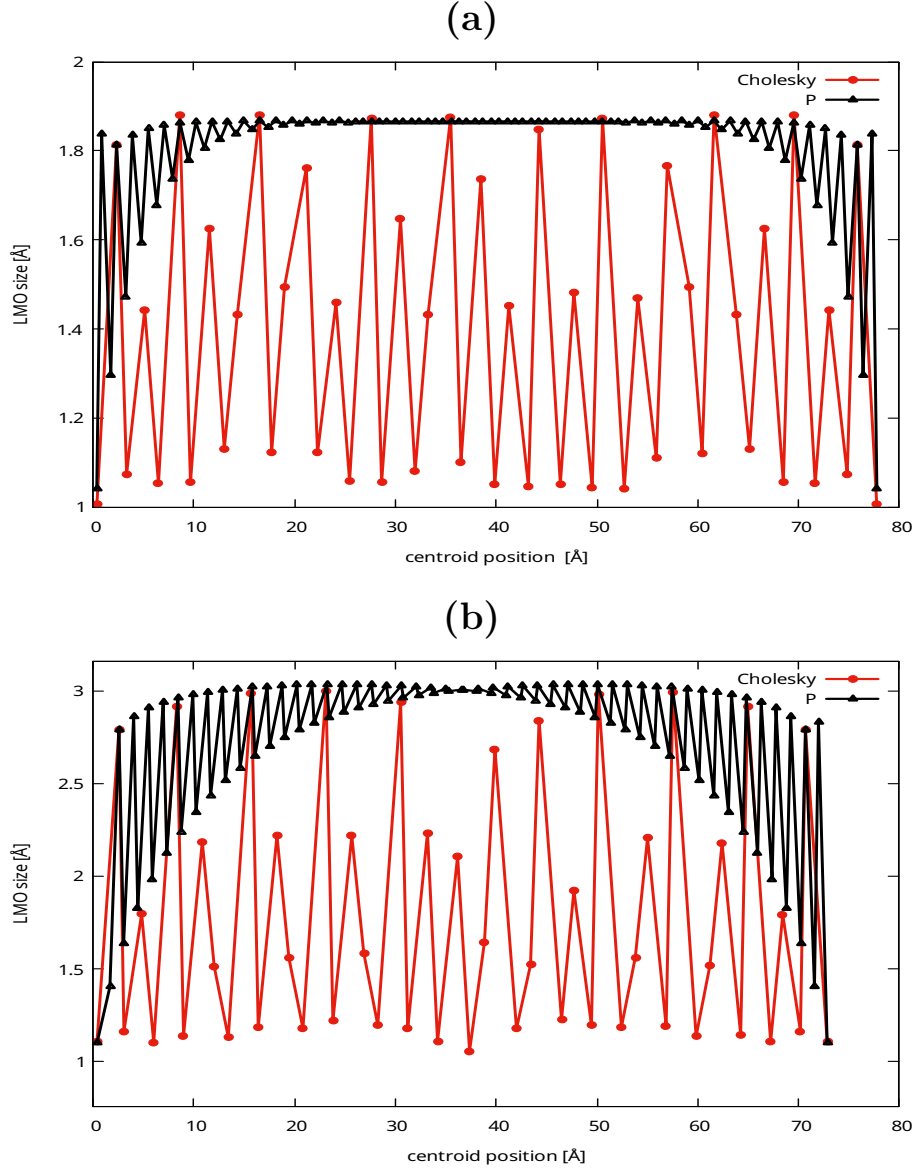
method of localization	metallic case	alternating case
Boys	1.3657	1.0974
P-LMOs	2.7395	1.8102
Pipek-Mezey	1.4262	1.1606
Edmiston-Ruedenberg	1.3678	1.0974

well the enhanced localizability in the case of alternating geometry, where the LMO sizes are smaller by 30-50%. Of the numbers shown, the Boys LMOs have the smallest sizes (the ER LMOs are similar though), which is natural as the Boys' procedure minimizes the sum of sizes. Comparing to Table I, however, one may observe that PS-LMOs have smaller size than Boys' ones. This is possible only because the Boys LMOs are obtained by minimizing the sizes with the orthogonality constraint, while the PS-LMOs are nonorthogonal. The P-LMOs are not orthogonal either but their sizes are larger by cca. 50%.

C. P-LMOs vs. Cholesky-LMOs

For the H_{100} chain with the alternating and the equidistant geometries the sizes of pristine and Cholesky-decomposed P-LMOs²³ show a great variety, as Fig.7 shows. For the alternat-

FIG. 7. Comparison of LMO sizes along the chain of 100 H atoms for Cholesky- and pristine P-LMOs for the alternating (a) and equidistant (b) geometries



ing geometry, the sizes vary for both types of LMOs between 1. and ~ 1.9 Å, but while the pristine P-LMOs show a simple regular pattern with smaller size at the surface and nearly constant and larger size at the bulk, the spread of Cholesky-LMOs exhibit a more irregular, oscillating pattern.

In the metallic case, the message is somewhat more complicated. First, sizes are larger reflecting weaker localizability of the system: they vary between 1.1 and 3.0 Å. The pristine P-LMOs are again smaller at the surface, their sizes actually are nearly the same as for the

alternating case, and are most extended at the bulk, with a slightly more oscillating pattern, than for the alternating system. The Cholesky-decomposed P-LMOs are strongly oscillating also in this case.

The average size of LMOs turns out to be 1.810 (alternating chain) and 2.739 (metallic chain) Å for the pristine LMOs, while the corresponding numbers for the Cholesky-decomposed LMOs are 1.389 and 1.780 Å, respectively.

The above conclusion, that Cholesky as well as standard iterative LMOs (cf. Table II.) are more compact for the model system studied here than pristine P-LMOs, is complemented by literature findings reporting that Cholesky-LMOs have larger orbital spreads⁸ than e.g. Boys or Pipek-Mezey LMOs.

D. P-LMOs vs. $P^{1/2}$ -LMOs

It was hinted in Section III. that localizability of P-LMOs may be enhanced by evaluating the square-root of the positive semidefinite matrix $\mathbf{P}$, which requires a little computational effort. This matrix is also a *razor*, therefore the thus obtained $P^{1/2}$ -LMOs will also be in the occupied subspace, where they also form a nonorthogonal, moreover redundant, set.

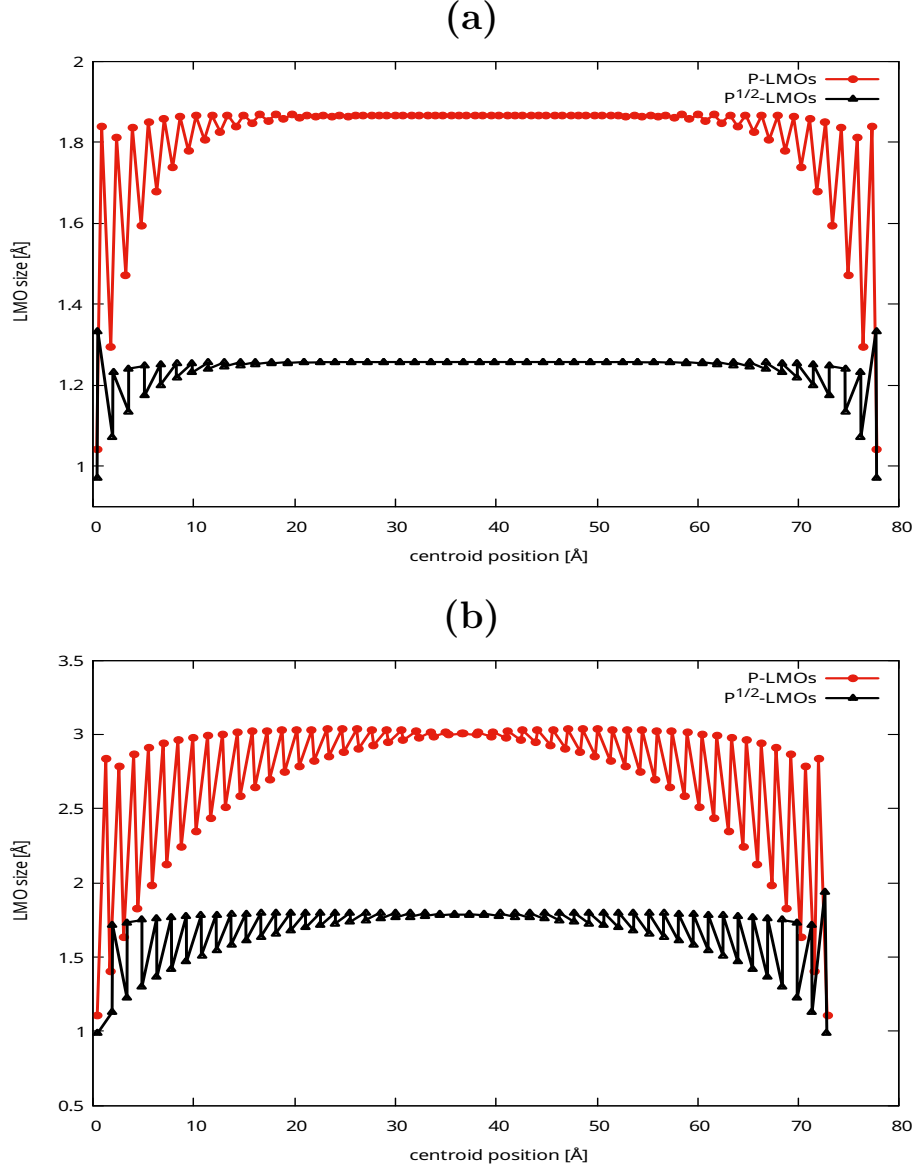
Figure 8. shows the comparison of P-LMO and $P^{1/2}$ -LMO sizes. It is apparent that the sizes of the latter type LMOs are significantly smaller indicating better locality of $P^{1/2}$ -LMOs. This is accompanied by a cca. 50% reduction of the size oscillation amplitudes at around the chain ends. This is valid even for the metallic-like geometry of the chain.

The better localized character of $P^{1/2}$ -LMOs is exhibited in Fig.9 showing LMO coefficients.

In the alternating case, the difference between the coefficients of the two kinds of LMOs is not very large, but the decrease of their absolute values when drawing the $P^{1/2}$ -LMOs is apparent at around the centroid of the LMOs, and it is significant at the tail shown in the inset.

In the metallic case the enhanced localization of $P^{1/2}$ -LMOs is obvious even at around the centroids, and the significantly faster decay of the coefficients is also convincing. This is accompanied by a reduction of the oscillation amplitudes with all $P^{1/2}$ -LMO coefficients having the same sign. Note that both LMOs are normalized to unity in metric $\mathbf{S}$.

FIG. 8. Sizes of P-LMOs and $P^{1/2}$ -LMOs for the H_{100} chain with alternating (a) and equidistant (b) geometries.

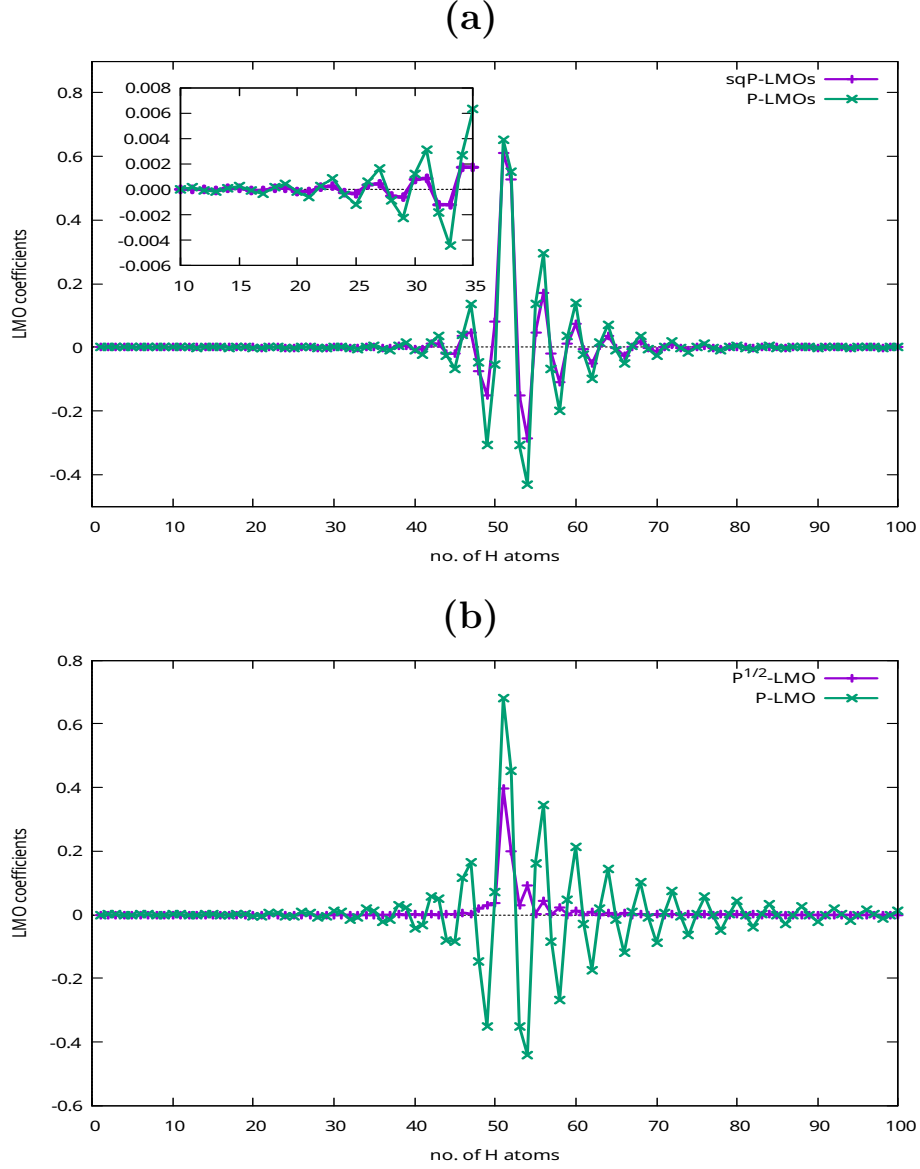


V. CONCLUSIONS

In Section II, it was suggested that P-LMOs may be more localized than the more widely used PS-LMOs. On the model system of H_{100} chains treated in a small basis set at different geometries, this expectation was fulfilled in some cases, but failed in others. In summary, the PS- and P-LMOs show similar characteristics regarding the decay, while the average size was found to be smaller for PS- than for P-LMOs for the systems studied.

A second expectation was formulated in Section III.: columns of matrix $\mathbf{P}^{1/2}$ are pre-

FIG. 9. Distribution of coefficients of P-LMOs and $P^{1/2}$ -LMOs for the H_{100} chain with alternating (a) and equidistant (b) geometries. The inset in (a) shows the asymptotic decays.



dicted to be significantly more localized than P-LMOs. This is indeed the case according to numerical examples, and the gain in the localized nature is significant. This opens a door for further investigations in this direction.

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