Supporting Information for:

“Charge Anisotropy of Nitrogen: Where Chemical Intuition Fails”

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In this Supporting Information, additional data pertaining to the scans for optimal EC placement are provided. In Section S-I the influence of different QM calculations on the 1D scan of ammonia and trimethylamine is discussed. In Section S-II we show how the fitted point charges are influenced by the EC position. Here, we discuss data for all 13 molecules considered in this study. In Section S-III additional figures for the 2D scans are provided to compare our results to the method presented by Horton et al.\textsuperscript{1}
S-I Influence of the QM level of theory on 1D scans

In this section of the Supporting Information, the influence of different QM calculations on the RMSE as a function of EC distance from the nitrogen is discussed. For this purpose 1D scans of the (pseudo)-C₃ axis of both ammonia and trimethylamine for optimal EC placement were performed. Scans were conducted for nine different QM levels for both molecules.

The results obtained for ammonia are depicted in Figure S1. It is visible that the values for the APC reference (r = 0) fall into two groups. The data obtained with the 6-31G* basis-set yield RMSE values of ≈ 1 kcal/mol, while for the other QM calculations the RMSE lies between 1.5 and 1.8 kcal/mol. This indicates that the APC description of ammonia is closer to the QM-ESPs generated with the 6-31G* basis set. Note that it is actually desired to obtain a small RMSE with respect to high-level QM calculations.

The splitting found for the APC approximations also persists if an EC is added. The 6-31G* calculations exhibit lower RMSE values for most parts of Figure S1. Only at approximately -1 Å the RMSEs of the non-6-31G* calculations drop below the 6-31G* RMSEs. Consequently, the introduction of an EC has a larger effect if more accurate QM calculations are performed. The difference between the 6-31G* and the non-6-31G* calculations could stem from the fact that the 6-31G* basis set introduces polarization functions only for the nitrogen and not the three hydrogen atoms, while all other basis sets use polarization functions for both species.

At any rate, for all QM calculations two minima are found when a single EC is introduced. One minimum at ≈ 1.5 Å and one at ≈ -1.0 Å. Interestingly enough, for all QM calculations the minimum at negative distances is lower suggesting very similar optimal locations for EC placement (−1.0 ≤ r ≤ −0.9 Å). For the 6-31G* calculations this minimum reduces the RMSE by ≈ 40% when compared to the APC reference. If more accurate QM calculations are...
performed, the placement of a single EC in this minimum reduces the RMSE even by ≈ 60% when compared to the respective APC reference. At the most favorable minimum two groups are also found for \( q_{EC} \), the charge of the EC. While calculations with the 6-31G\(^*\) basis set yield \(-0.082 \leq q_{EC} \leq -0.079 \) e, all other calculations yield ECs with larger magnitudes \((-0.188 \leq q_{EC} \leq -0.164 \) e).

\[ \text{Figure S1} \] RMSE of the 1D scan for ammonia. At \( r = 0 \) the RMSE corresponds to the plain atomic point charge (APC) reference. The different data sets correspond to different QM levels of theory as indicated in the legend.

In Figure S2 the results are shown for trimethylamine. Here, the situation is more complex. Similar RMSE data are found for B3LYP calculations when the basis sets aug-cc-pVDZ, aug-cc-pVTZ, or 6-311++G(3df,3pd) are used. The results for HF and CCSD with the 6-31G\(^*\) basis set are located at lower RMSE, but they are similar to each other. All other QM calculations yield RMSE values between those two groups. Despite the added complexity, when compared
to ammonia still two minima are found in all cases. A rather broad minimum appears between −2.0 and −1.0 Å and a more localized minimum is visible at ≈ 2.0 Å. Yet, the lowest minimum is not the same for all QM calculations. The B3LYP calculations yield the lower minimum at negative distances (−1.6 ≤ r ≤ −1.4 Å), while in all other cases the minimum at positive distances is lower (1.9 ≤ r ≤ 2.1 Å). That is, depending on the QM calculation a different optimal EC location is proposed. In contrast to the location of the minimum, the charges obtained for the EC at the respective minima do not fall into two separate groups, but rather are distributed in the range −0.020 ≤ qEC ≤ −0.053 e. For the B3LYP calculations, the optimal EC placement leads to a RMSE reduction between 30 and 35%, for CCSD calculations between 20 and 30%, and for HF calculations between 15 and 25% when compared to the respective APC reference.

Note that QM-ESP calculations with basis-sets larger than 6-31G* yield similar results (cf. Figure 3A in the main document). In addition, the optimal location for the EC placement for ammonia is insensitive to the QM calculation used. For trimethylamine, different locations are proposed by different QM variants. While all B3LYP calculations indicate the optimal spot for EC placement in the direction of the methyl groups, all other calculations suggest that the optimal spot is in the lone-pair direction. In any case, all QM variants used indicate two minima
at similar locations for trimethylamine. Moreover, irrespective of the optimal EC location the improvement of the ESP upon EC introduction is small when compared to ammonia.

**Figure S2** RMSE of the 1D scan for trimethylamine. At $r = 0$ the RMSE corresponds to the plain atomic point charge (APC) reference. The different data sets correspond to different QM levels of theory as indicated in the legend.
S-II Influence of the EC position on the point charges

1D scans

In this section, we provide additional figures related to the 1D scans of ammonia, trimethylamine and triethylamine. In these figures (Figures S3–S5) the values of all point charges are shown as a function of EC distance $r$ from the nitrogen atom. The data shown correspond to QM calculations at B3LYP/6-311++G(3df,3pd) level. For ammonia, the results are shown in Figure S3. The EC itself is negative at almost all scanned distances, only at positive $r \leq 0.7 \, \text{Å}$ the EC assumes a positive charge. Conversely, the nitrogen point charge is negative at all distances except for the point scanned at $r = -0.1 \, \text{Å}$. The hydrogen point charge is positive and comparably small ($< 0.6 \, \text{e}$) for all scanned distances $r$.

Figure S3 Charge of the EC and the point charges on the atom centers for the 1D scan of ammonia. The inset shows the full data for the EC and the nitrogen atom. At $r = 0$ the charges correspond to the plain atomic point charge (APC) reference. The results are based on B3LYP/6-311++G(3df,3pd) calculations.
Similar data are shown for trimethylamine in Figure S4. Here all point charges (EC, N, C and H) are in the range ± 0.1 e. The EC is again negative for all negative distances and changes sign at positive distances. In contrast to ammonia, the nitrogen point charge is positive in the majority of cases. Only at positive \( r \leq 0.7 \) Å, a negative point charge is associated with the nitrogen atom. The hydrogen and the carbon point charges show little variation. The former is positive for all scanned \( r \), while the latter is negative in all cases.

![Figure S4](image)

**Figure S4** Charge of the EC and the point charges on the atom centers for the 1D scan of trimethylamine. At \( r = 0 \) the charges correspond to the plain atomic point charge (APC) reference. The results are based on B3LYP/6-311++G(3df,3pd) calculations.

The data for triethylamine is shown in Figure S5. As in the previous two cases, the EC is negative at negative \( r \) and it changes sign at positive \( r \). The point charge of the nitrogen atom shows a similar trend as for ammonia, i.e., it is negative for the majority of scanned distances. Positive values for the nitrogen atom are found at negative \( r \geq -1.1 \) Å. In the CH\(_2\) group, the hydrogen as well as the carbon point charges can be positive or negative depending on the
position of the EC. While the carbon point charge is predominantly negative at negative $r$ and predominantly positive at positive $r$, the opposite is observed for the hydrogen point charges. The CH$_3$ group point charges change little with EC position. The carbon point charge is always negative and the point charges of the hydrogen atoms are always positive.

For these three molecules, the point charges are relatively small for all EC locations. Only for ammonia and triethylamine, the charges can exceed a magnitude of 1.5 e if the EC is within 0.3 Å of the nitrogen atom.

![Figure S5](image)

**Figure S5** Charge of the EC and the point charges on the atom centers for the 1D scan of triethylamine. The inset shows the full data for the EC and the nitrogen atom. At $r = 0$ the charges correspond to the plain atomic point charge (APC) reference. The results are based on B3LYP/6-311++G(3df,3pd) calculations.
In this section, additional figures related to the 2D scans of the primary and secondary amines as well as the amides are provided. In particular, these figures show the influence of the EC position (defined by $r$ and $\phi$; cf. Figure 2 in the main document) on the point charges present in each molecule. Figure S6 shows polar heat maps for the RMSE and the corresponding charges for methylamine and ethylamine. The RMSE plots are color coded as in the main document and the color scale for the charge plots is set to always span the range $-1.5$ to $1.5$ e, red indicating positive values and blue indicating negative values. This range was chosen to emphasize variations of smaller charges. Charges exceeding a magnitude of $1.5$ e are not explicitly highlighted. These rather large charges are only found when the EC gets close to atom centers. Figure S6 reveals that the EC charge behaves similar in both molecules. It is positive around the C-N bond and negative in other areas. For methylamine, the positive area extends upward of the C-N bond, while the positive area extends up- and downward for ethylamine. The nitrogen point charge behaves very similar in both cases, assuming mostly negative charges except when the EC is located very close to the nitrogen. In addition, the charge of the carbon bound to the nitrogen changes significantly with the EC placement. While positive and negative areas are almost equal in size for methylamine, positive charges dominate in ethylamine. The charges of the hydrogen bound to the nitrogen in both molecules as well as the charges of the CH$_3$ hydrogens in ethylamine show little variation with EC placement. The point charge of the CH$_3$ carbon of ethylamine shows some variation, but it is always negative. Charges of the hydrogen atoms of the CH$_3$ group in methylamine and the CH$_2$ group in ethylamine are small for all EC locations, but a change in sign is noted.
Figure S6 RMSE and charge of the EC and the point charges on the atom centers of the 2D scans for methylamine and ethylamine. The two columns show the data for the two different molecules. The top row shows the RMSE (cf. Figure 7 in the main document). The other rows show the charges of the EC and the point charges on the atom centers as a function of EC location. The color scales for the charges always span the range $-1.5$ to $1.5\, \text{e}$. The results are based on B3LYP/6-311++G(3df,3pd) calculations.
The data for the secondary amines is shown in Figure S7. For all four molecules the EC, the nitrogen point charge and the hydrogen point charge of the amine group behave similarly. The EC is negative around the H-N bond and positive in other areas. For pyrrolidine, the negative area extends only upward from the H-N bond, while it extends in both directions for the other three secondary amines. The nitrogen point charge is mostly negative, but it can be positive for some locations where the EC is negative. The hydrogen point charge of the amine group is predominantly positive, except when the EC is located very close to this hydrogen atom. For dimethyl- and diethylamine, the terminal carbon point charges are negative and the corresponding hydrogen point charges are positive for all EC locations. However, both types of charges present in the CH₂ group of diethylamine can change sign depending on the EC position. This is similar to what was observed for the CH₂ group of ethylamine (cf. Figure S6).

In aziridine, the CH₂ group point charges show little variation. The carbon charges are mostly negative, except for a small sector, while the hydrogen charges are always positive. For pyrrolidine, the point charges of both types of CH₂ carbons can change sign depending on the EC location, as do the hydrogen point charges of the CβH₂ group. In contrast, the hydrogen atoms of the CαH₂ group always carry positive point charges.

The results for formamide and acetamide are shown in Figure S8. In both cases, positive ECs are found above the C-N bond while negative EC charges are found below it. For formamide, this area extends up to the O-C bond, while in acetamide a crossing of the C-C bond causes the EC to change sign. Almost all other point charges show little dependence on the EC position. Only the point charge associated with the carbonyl hydrogen of formamide changes sign if the EC approaches its location. Note that since the hydrogens bound to the nitrogen share the atom type, they have equal point charges. Therefore, the approach of the EC to either one of the two hydrogen atoms is not reflected in the charge plots.
Figure S7 RMSE and charge of the EC and the point charges on the atom centers of the 2D scans for dimethylamine, diethylamine, aziridine, and pyrrolidine. The four columns show the data for the four different molecules. The top row shows the RMSE (cf. Figure 8 in the main document). The other rows show the charges of the EC and the point charges on the atom centers as a function of EC location. The results are based on B3LYP/6-311++G(3df,3pd) calculations.
Figure S8 RMSE and charge of the EC and the point charges on the atom centers of the 2D scans for formamide and acetamide. The two columns show the data for the two different molecules. The top row shows the RMSE (cf. Figure 9 in the main document). The other rows show the charges of the EC and the point charges on the atom centers as a function of EC location. The results are based on B3LYP/6-311++G(3df,3pd) calculations.
In Figure S9 the results for N-methylformamide are presented. For this molecule, we also studied the influence of internal rotations on the ESP fitting. Hence, data for three different rotamers of N-methylformamide are shown in Figure S9. The first column shows the RMSE of the 2D scans of the rotamer considered in the main manuscript (cf. Figure 9). Here a hydrogen of the methyl group and the carbonyl group are eclipsed (0°). The second column shows the RMSE for a methyl group rotation of 30° and the third column shows the RMSE for a methyl group rotation of 60°. While the APC RMSE is similar in all three structures, it is found that the area between the methyl and the carbonyl group is significantly affected by the rotation. In the eclipsed case, an EC in this area can improve the ESP approximation by ≈ 50%, while only ≈ 20% can be achieved for the other two rotamers. Moreover, the area where such an improvement is possible shrinks as the methyl group is rotated. In contrast, the area around the N-H bond is hardly affected by the rotation and an EC in this area can improve the ESP approximation by ≈ 50% in all cases. This suggests that this area is to be favored for EC placement since it significantly enhances the ESP description for all rotamers considered.

The behavior of the eight corresponding point charges is shown in the remaining rows. For all rotamers, the EC is positive above the C-N-C chain, negative around the N-H bond, and positive beyond this hydrogen. Similarly, the point charges of the nitrogen and the hydrogen bound to it change little for the different rotamers. In all three cases, the nitrogen charge is predominantly negative, and the hydrogen charge is predominantly positive. Only if the EC is located around the N-H bond and its extension beyond the hydrogen, the nitrogen point charge becomes positive. Once the EC approaches the hydrogen, its charge also changes sign. The point charges corresponding to the carbonyl group show little change when either the EC position or the CH₃ rotation is changed. The point charges of the CH₃ group show some dependence on rotation. The carbon point charge initially (0°) depends quite strongly on EC placement, including several changes in sign. For a rotation of 30° the point charge is negative.
in almost all areas and for a rotation of $60^\circ$ the carbon point charge is negative everywhere. The corresponding hydrogen point charges do not show changes in sign (they are always positive), but their magnitude increases as the CH$_3$ rotation is increased from 0 to $60^\circ$.

Figure S10 shows polar heat maps for the RMSE and the corresponding charges for N-methylacetamide. Similar to N-methylformamide the EC and the point charges corresponding to the nitrogen, its hydrogen, the carbonyl carbon and the N-methyl carbon are significantly influenced by the EC location. The oxygen point charge is almost unaffected as are the point charges of the methyl group, which is connected to the carbonyl C. The EC charge is also reminiscent of the other amides, i.e., it is positive above the C(carbonyl)-N bond and negative below it. In addition, the point charge of the nitrogen, which is positive only if the EC is placed around the N-H bond, and the corresponding hydrogen point charge behave similar as in the other amides.
The three columns show the data for the three different rotamers of N-methylformamide. Torsions of the N-C(methyl) bond considered are 0°, 30° and 60° – this is illustrated using Newman projections in the figure. The top row shows the RMSE (cf. Figure 9 in the main document). The coloring indicates the RMSE and the maximum of the color scale is the RMSE of the plain atomic point charge (APC) reference. The other rows show the charges of the EC and the point charges on the atom centers as a function of EC location. The results are based on B3LYP/6-311++G(3df,3pd) calculations.

Figure S9 RMSE and charge of the EC and the point charges on the atom centers of the 2D scans for N-methylformamide.
Figure S10 RMSE and charge of the EC and the point charges on the atom centers of the 2D scans for N-methylacetamide. The RMSE is shown at the top right (cf. Figure 9 in the main document). The coloring indicates the RMSE and the maximum of the color scale is the RMSE of the plain atomic point charge (APC) reference. The other panels show the charges of the EC and the point charges on the atom centers as a function of EC location. The results are based on B3LYP/6-31++G(3df,3pd) calculations.
Results for minimal RMSE

Table S1 Summary of the optimal EC locations and the corresponding point charges for the 13 molecules considered in this study. Charges are rounded to the third decimal place. Therefore, the sum of the charges is not necessarily exactly zero.

| Ammonia, primary, secondary and tertiary amines | RMSE / kcal/mol | EC | N group | CH3 group | CH2 group |
|------------------------------------------------|-----------------|-----|---------|-----------|----------|
|                                                | r / Å | φ / ° | qEC    | qN / e    | qH / e   | qC / e  | qH / e | qC / e  | qH / e |
| Ammonia                                       | 0.601 | −0.9  | −0.188 | −1.108 | 0.432 |
| Trimethylamine                                 | 0.477 | −1.4  | −0.048 | 0.191  | −0.810 | 0.254 |
| Triethylamine                                  | 0.504 | −0.8  | −0.433 | 0.116  | −0.501 | 0.144 | −0.113 | 0.144 |
| Methylamine                                    | 0.620 | 0.7   | 10 0.823 | −1.415 | 0.431 | −0.835 | 0.188 |
| Ethylamine                                     | 0.412 | 2.0   | 15 0.268 | −1.047 | 0.372 | −0.845 | 0.201 | 0.529 | 0.141 |
| Dimethylamine                                  | 0.638 | 1.5   | 85 0.125 | 0.200  | 0.143 | −0.553 | 0.148 |
| Diethylamine                                   | 0.520 | 1.7   | 170 0.096 | −0.878 | 0.389 | −0.340 | 0.089 | 0.317 | −0.024 |

| Cyclic amines                                  | RMSE / kcal/mol | EC | N group | C6H5 group | C3H3 group |
|------------------------------------------------|-----------------|-----|---------|------------|-----------|
|                                                | r / Å | φ / ° | qEC    | qN / e    | qC / e  | qH / e | qC / e  | qH / e |
| Aziridine                                      | 0.539 | 0.5   | 250 0.909 | −1.115 | 0.379 | −0.390 | 0.152 |
| Pyrrolidine                                    | 0.414 | 1.1   | 250 0.763 | −0.782 | 0.357 | −0.358 | 0.154 | −0.347 | 0.115 |

| Amides                                         | RMSE / kcal/mol | EC | N group | Carbonyl group | CH3 group on C | CH3 group on N |
|------------------------------------------------|-----------------|-----|---------|----------------|----------------|----------------|
|                                                | r / Å | φ / ° | qEC    | qN / e    | qC / e  | qH / e | qC / e  | qH / e | qC / e  | qH / e |
| Formamide                                      | 0.400 | 1.1   | 20 0.218 | −0.979 | 0.417 | 0.429 | −0.548 | 0.046 |
| Acetamide                                      | 0.274 | 1.2   | 160 0.029 | −1.045 | 0.406 | 0.987 | −0.621 | −0.795 | 0.211 |
| N-methyl-formamide                             | 0.295 | 0.3   | 250 −2.223 | 1.706 | 0.671 | 0.242 | −0.499 | 0.099 | −0.364 | 0.123 |
| 30°                                            | 0.322 | 0.4   | 250 −1.737 | 1.173 | 0.720 | 0.271 | −0.504 | 0.089 | −0.471 | 0.153 |
| 60°                                            | 0.297 | 0.5   | 250 −1.410 | 0.820 | 0.752 | 0.295 | −0.503 | 0.079 | −0.601 | 0.189 |
| N-methyl-acetamide                             | 0.240 | 0.4   | 260 −1.252 | 0.638 | 0.591 | 0.770 | −0.599 | −0.782 | 0.216 | −0.481 | 0.155 |
Table S2 Summary of the optimal EC locations and the corresponding point charges for the 13 molecules considered in this study, where \( r < 1 \) Å. Charges are rounded to the third decimal place. Therefore, the sum of the charges is not necessarily exactly zero.

| Ammonia, primary, secondary and tertiary amines | RMSE / kcal/mol | EC \( r / \text{Å} \) | \( \phi / ^\circ \) | \( q_{EC} \) | \( q_{N} / e \) | \( q_{\text{H}} / e \) | \( q_{C_{\alpha}} / e \) | \( q_{C_{\beta}} / e \) | \( q_{\text{H}} / e \) | \( q_{\text{H}} / e \) |
|-----------------------------------------------|-----------------|-------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Ammonia                                      | 0.601           | –0.9              | –0.188          | –1.108          | 0.432           |                 |
| Trimethylamine                                | 0.483           | –0.9              | –0.088          | 0.202           | –0.799          | 0.254           |
| Triethylamine                                 | 0.504           | –0.8              | –0.433          | 0.116           | –0.501          | 0.144           | –0.113          | 0.144           |
| Methylamine                                   | 0.620           | 0.7               | 0.823           | –1.415          | 0.431           | –0.835          | 0.188           |
| Ethylamine                                    | 0.649           | 0.5               | 2.406           | –0.851          | 0.490           | –0.365          | 0.090           | 0.198           | 0.057           |
| Dimethylamine                                 | 0.731           | 0.9               | 1.800           | –0.766          | 0.469           | –0.453          | 0.164           |
| Diethylamine                                  | 0.566           | 0.9               | 1.756           | –0.322          | –0.074          | –0.161          | 0.051           | 0.061           | 0.032           |

| Cyclic amines                                 | RMSE / kcal/mol | EC \( r / \text{Å} \) | \( \phi / ^\circ \) | \( q_{EC} \) | \( q_{N} / e \) | \( q_{\text{H}} / e \) | \( q_{C_{\alpha}} / e \) | \( q_{C_{\beta}} / e \) | \( q_{\text{H}} / e \) | \( q_{\text{H}} / e \) |
|-----------------------------------------------|-----------------|-------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Aziridine                                     | 0.539           | 0.5               | 2.506           | 0.909           | –1.115          | 0.379           | –0.390          | 0.152           |
| Pyrrolidine                                   | 0.428           | 0.8               | 2.456           | 0.798           | –0.967          | 0.386           | –0.303          | 0.136           | –0.295          | 0.108           |

| Amides                                        | RMSE / kcal/mol | EC \( r / \text{Å} \) | \( \phi / ^\circ \) | \( q_{EC} \) | \( q_{N} / e \) | \( q_{\text{H}} / e \) | \( q_{C_{\alpha}} / e \) | \( q_{C_{\beta}} / e \) | \( q_{\text{H}} / e \) | \( q_{\text{H}} / e \) |
|-----------------------------------------------|-----------------|-------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Formamide                                     | 0.404           | 0.9               | 0.021           | –1.014          | 0.420           | 0.445           | –0.536          | 0.043           |
| Acetamide                                     | 0.275           | 0.9               | 1.096           | 0.442           | 1.024          | –0.619          | –0.575          | 0.167           |
| N-methyl-formamide                            | 0.295           | 0.3               | 1.706           | 0.671           | 0.242           | –0.499          | 0.099           | –0.364          | 0.123           |
| 30°                                           | 0.322           | 0.4               | 1.173           | 0.720           | 0.271           | –0.504          | 0.089           | –0.471          | 0.153           |
| 60°                                           | 0.297           | 0.5               | 0.820           | 0.752           | 0.295           | –0.503          | 0.079           | –0.601          | 0.189           |
| N-methyl-acetamide                            | 0.240           | 0.4               | 0.638           | 0.591           | 0.770           | –0.599          | –0.782          | 0.216           | –0.481          | 0.155           |
S-III Comparison to literature data

Figures S11 and S12 are reproductions of Figures 7 and 8 of the main document, respectively. Shown are the RMSE results of the 2D scans for methyl- and ethylamine (Figure S11) as well as dimethyl-, diethylamine, aziridine and pyrrolidine (Figure S12). Added to these figures are black arrows indicating the vector on which the first EC is placed according to the approach presented by Horton et al. In no case these vectors coincide with one of the minima identified in the present survey.

**Figure S11** RMSE of the 2D scans for methylamine (A) and ethylamine (B). Here, the C-N bond lies in the scanned plane (cf. Figure 2C and D in the main document). The coloring indicates the RMSE and the maximum of the color scale is the RMSE of the plain atomic point charge (APC) reference. The results are based on B3LYP/6-311++G(3df,3pd) calculations. The black arrow indicates the direction in which the first EC would be placed according to the method introduced by Horton et al.
Figure S12 RMSE of the 2D scans for dimethylamine (A), diethylamine (B), aziridine (C), and pyrrolidine (D). Here, the H-N bond lies in the scanned plane (cf. Figure 2C and D in the main document). The coloring indicates the RMSE and the maximum of the color scale is the RMSE of the plain atomic point charge (APC) reference. Note that for clarity the CH₃ group is not shown in the case of diethylamine (B). The results are based on B3LYP/6-311++G(3df,3pd) calculations. The black arrow indicates the direction in which the first EC would be placed according to the method introduced by Horton et al.¹

References

1. Horton, J. T.; Allen, A. E.; Dodda, L. S.; Cole, D. J., QUBEKit: automating the derivation of force field parameters from quantum mechanics. J. Chem. Inf. Model. 2019, 59 (4), 1366–1381.