# Supplementary Information for "Exploring Accuracy Limits of Predictions of the ${ }^{1} H$ NMR Chemical Shielding Anisotropy in the Solid State" by Czernek and Brus (2019) 

## Content (ten pages in total):

raw data for Table 1 of the main text ... pages 2 (isotropic) and 3 (eigenvalues) raw data for Table 2 of the main text ... pages 2 (isotropic) and 3 (eigenvalues) raw data for Table 3 of the main text ... page 4
details of the orientation of the imidazole ${ }^{15} \mathrm{~N}$ chemical shielding tensors ... page 4 comparisons of the ${ }^{1} \mathrm{H}$ chemical shielding tensor orientations of citric acid in crystal/molecular frames ... page 5
distance-dependence of the ${ }^{1} \mathrm{H}$ NMR data the in the phenol-water dimer ... page 6
projections of the ${ }^{1} \mathrm{H}$ chemical shielding tensors of malonic acid onto the molecular frame ...
pages 7 - 10

Table SI1. The ${ }^{1} \mathrm{H}$ isotropic chemical shift/shielding data (in ppm ) for maleic and malonic acids.

| site | exptl chemical shift <br> as used here** | GIPAW-PBE <br> $\sigma^{\text {iso }}$ | GIPAW-revPBE <br> $\sigma^{\text {iso }}$ |
| :---: | :---: | :---: | :---: |
| H1 in maleic acid | 10.95 | 15.2260 | 15.9568 |
| H2 in maleic acid* | 4.0167 | 23.6430 | 23.8516 |
| H3 in maleic acid* | 4.0167 | 23.4383 | 23.6941 |
| H4 in maleic acid | 13.0167 | 12.9602 | 13.6646 |
| H1 in malonic acid | 10.7167 | 15.2486 | 16.2169 |
| H2 in malonic acid | 10.05 | 15.4284 | 16.3289 |
| H3 in malonic acid | 1.3833 | 27.2185 | 27.5132 |
| H4 in malonic acid | 1.5833 | 27.0794 | 27.2931 |

* H2, H3 experimentally unresolved
** after conversion from data referenced to adamantane in references [10] and [11] of the main text

Table SI2. The ${ }^{1} \mathrm{H}$ isotropic chemical shift/shielding data (in ppm) for L-histidine hydrochloride monohydrate.

| site | exptl chemical shift | GIPAW-PBE $\sigma^{\text {iso }}$ | GIPAW-revPBE $\sigma^{\text {iso }}$ |
| :---: | :---: | :---: | :---: |
| H bound to $\mathrm{C} \alpha$ | 3.5 | 27.7943 | 28.1004 |
| two ${ }^{*}$ H bound to $\mathrm{C} \beta$ | 3.3 | 27.5628 | 27.8429 |
| H bound to $\mathrm{C} \varepsilon$ | 9.3 | 21.1359 | 21.2404 |
| H bound to $\mathrm{C} \delta$ | 8.0 | 22.8031 | 23.0594 |
| H (ammonium) | 8.6 | 21.5953 | 22.0039 |
| H bound to $\mathrm{N} \delta$ | 16.8 | 12.8670 | 12.8656 |
| H bound to $\mathrm{N} \varepsilon$ | 12.6 | 17.4304 | 17.8841 |

* experimentally unresolved

Table SI3. The ${ }^{13} \mathrm{C}$ isotropic chemical shift/shielding data (in ppm ) for L-histidine hydrochloride monohydrate.

| site | exptl chemical shift | GIPAW-PBE $\sigma^{\text {iso }}$ | GIPAW-revPBE $\sigma^{\text {iso }}$ |
| :---: | :---: | :---: | :---: |
| $\mathrm{C}^{\prime}$ | 173.2 | -5.6730 | -2.6127 |
| $\mathrm{C} \alpha$ | 54.1 | 116.4630 | 117.2207 |
| $\mathrm{C} \beta$ | 26.0 | 145.0781 | 145.6808 |
| $\mathrm{C} \gamma$ | 128.7 | 39.5322 | 41.7607 |
| $\mathrm{C} \delta$ | 136.3 | 34.9954 | 37.3542 |
| $\mathrm{C} \varepsilon$ | 119.4 | 50.2050 | 52.1428 |

Table SI4. The principal components (in ppm) of ${ }^{15} \mathrm{~N}$ chemical shift/shielding tensors in L-histidine hydrochloride monohydrate ( $x x, y y, z z$ respectively denote the most shielded, the mid-shielded, and the least shielded eigenvalue).

| site | exptl $\delta_{i i}$ | GIPAW-PBE $\sigma_{i i}$ | GIPAW-revPBE $\sigma_{i i}$ |
| :---: | :---: | :---: | :---: |
| $x x$ of $\mathrm{N} \delta$ | 38.8 | 167.3731 | 165.0983 |
| $y y$ of $\mathrm{N} \delta$ | 198.1 | -8.5969 | -10.7169 |
| $z z$ of $\mathrm{N} \delta$ | 260.5 | -62.8181 | -65.8502 |
| $x x$ of $\mathrm{N} \varepsilon$ | 35.1 | 172.6674 | 171.852 |
| $y y$ of $\mathrm{N} \varepsilon$ | 170.1 | 22.3478 | 15.4684 |
| $z z$ of $\mathrm{N} \varepsilon$ | 251.3 | -50.2537 | -54.7112 |

Table SI5. The principal components (in ppm ) of ${ }^{1} \mathrm{H}$ chemical shift/shielding tensors in maleic and malonic acids ( $x x, y y, z z$ respectively denote the least shielded, the mid-shielded, and the most shielded eigenvalue).

| component, site | expt1** $\delta_{i i}$ | GIPAW-PBE $\sigma_{i i}$ | GIPAW-revPBE $\sigma_{i i}$ |
| :---: | :---: | :---: | :---: |
| $x x$ of H1 in maleic acid | 19.45 | 6.5824 | 7.6042 |
| $y y$ of H1 in maleic acid | 15.15 | 8.7812 | 9.8148 |
| $z z$ of H1 in maleic acid | -1.75 | 30.3144 | 30.4515 |
| $x x$ of H2 in maleic acid* | 7.05 | 21.0694 | 21.332 |
| $y y$ of H2 in maleic acid* | 3.95 | 23.2329 | 23.4028 |
| $z z$ of H2 in maleic acid* | 1.05 | 26.6266 | 26.8199 |
| $x x$ of H3 in maleic acid* | 7.05 | 20.6229 | 20.9715 |
| $y y$ of H3 in maleic acid* | 3.95 | 23.5430 | 23.675 |
| $z z$ of H3 in maleic acid* | 1.05 | 26.1491 | 26.4359 |
| $x x$ of H4 in maleic acid | 22.95 | 2.2770 | 3.3128 |
| $y y$ of H4 in maleic acid | 18.15 | 6.1046 | 7.1191 |
| $z z$ of H4 in maleic acid | -2.05 | 30.499 | 30.562 |
| $x x$ of H1 in malonic acid | 19.65 | 5.3874 | 7.0026 |
| $y y$ of H1 in malonic acid | 14.55 | 8.8215 | 9.9064 |
| $z z$ of H1 in malonic acid | -2.05 | 31.5369 | 31.7418 |
| $x x$ of H2 in malonic acid | 18.55 | 5.5659 | 7.0737 |
| $y y$ of H2 in malonic acid | 14.15 | 8.8986 | 9.9876 |
| $z z$ of H2 in malonic acid | -2.55 | 31.8206 | 31.9255 |
| $x x$ of H3 in malonic acid | 3.65 | 24.9135 | 25.2372 |
| $y y$ of H3 in malonic acid | 2.35 | 26.2209 | 26.4656 |
| $z z$ of H3 in malonic acid | -1.85 | 30.5212 | 30.8368 |
| $x x$ of H4 in malonic acid | 3.85 | 24.3205 | 24.6039 |
| $y y$ of H4 in malonic acid | 1.85 | 26.5351 | 26.6388 |
| $z z$ of H4 in malonic acid | -0.95 | 30.3826 | 30.6367 |

* H2, H3 experimentally unresolved
** after conversion from data referenced to adamantane in references [10] and [11] of the main text

Table SI6. The principal components (in ppm) of ${ }^{1} \mathrm{H}$ chemical shift/shielding tensors in citric acid ( $x x, y y, z z$ respectively denote the least shielded, the mid-shielded, and the most shielded eigenvalue).

| component, site | exptl <br> $\delta_{i i}{ }^{*}$ | GIPAW-PBE <br> $\sigma_{i i}$ | GIPAW-revPBE <br> $\sigma_{i i}$ | GIAO-B3LYP <br> $\sigma_{i i}$ |
| :---: | :---: | :---: | :---: | :---: |
| $x x$ of H5 | 22.2 | 2.3769 | 3.9860 | -0.1642 |
| $y y$ of H5 | 22.2 | 5.9180 | 7.0273 | 9.7398 |
| $z z$ of H5 | -2.7 | 33.2971 | 33.4162 | 34.9793 |
| $x x$ of H6 | 18.825 | 9.3172 | 10.4805 | 10.2952 |
| $y y$ of H6 | 15.075 | 11.8739 | 13.3139 | 12.5348 |
| $z z$ of H6 | -1.8 | 32.6174 | 32.8246 | 35.0316 |
| $x x$ of H7 | 17.5 | 7.2983 | 9.0027 | 8.0095 |
| $y y$ of H7 | 15.0 | 12.7725 | 14.5510 | 13.2200 |
| $z z$ of H7 | -2.5 | 31.8768 | 31.7619 | 33.4513 |
| $x x$ of H8 | 13.54 | 17.2049 | 18.0584 | 16.6294 |
| $y y$ of H8 | 10.86 | 20.8799 | 21.6416 | 20.5776 |
| $z z$ of H8 | -7.9 | 38.8302 | 38.9283 | 39.0381 |

* Haeberlen notation was used in reference [15] of the main text

Table SI7. The orientation of the ${ }^{15} \mathrm{~N}$ chemical shielding tensors of the $\mathrm{N} \delta$ and $\mathrm{N} \varepsilon$ sites in L-histidine hydrochloride monohydrate (the xyz coordinate system is as described in the caption of Figure 3 of reference [13] of the main text, and $x x, y y, z z$ respectively denote the least shielded, the mid-shielded, and the most shielded eigenvalue).

| angle | exptl | GIPAW-PBE |
| :---: | :---: | :---: |
| between $z$ and the eigenvector <br> associated with $x x$ of $\mathrm{N} \delta$ | $0.0^{\circ}$ | $1.3^{\circ}$ |
| between $x$ and the eigenvector <br> associated with $z z$ of $\mathrm{N} \delta$ | $14.2^{\circ}$ | $16.5^{\circ}$ |
| between $y$ and the eigenvector <br> associated with $y y$ of $\mathrm{N} \delta$ | $14.2^{\circ}$ | $16.5^{\circ}$ |
| between $x$ and the $\mathrm{N} \delta-\mathrm{H} \delta$ <br> bond vector | $5.0^{\circ}$ | $1.8^{\circ}$ |
| between $z$ and the eigenvector <br> associated with $x x$ of $\mathrm{N} \varepsilon$ | $0.7^{\circ}$ | $1.5^{\circ}$ |
| between $x$ and the eigenvector <br> associated with $z z$ of $\mathrm{N} \varepsilon$ | $13.6^{\circ}$ | $13.7^{\circ}$ |
| between $y$ and the eigenvector <br> associated with $y y$ of $\mathrm{N} \varepsilon$ | $13.7^{\circ}$ | $13.8^{\circ}$ |
| between $x$ and the $\mathrm{N} \varepsilon-\mathrm{H} \varepsilon$ <br> bond vector | $2.0^{\circ}$ | $3.8^{\circ}$ |

Table SI8. Angles (in degrees) between the eigenvectors associated with the most shielded eigenvalue of $\{\mathrm{H} 5, \mathrm{H} 6, \mathrm{H} 7, \mathrm{H} 8\}$ protons in citric acid discussed in the main text (values in upper triangle are from the GIAO-B3LYP/6-311++G(2d,2p) calculation on the cluster model, values in lower triangle: GIPAW-PBE for the periodic structure).

| cluster / periodic | $\overrightarrow{\xi_{3}}$ of H 5 | $\overrightarrow{\xi_{3}}$ of H 6 | $\overrightarrow{\xi_{3}}$ of H 7 | $\overrightarrow{\xi_{3}}$ of H 8 |
| :---: | :---: | :---: | :---: | :---: |
| $\overrightarrow{\xi_{3}}$ of H5 | $0 / 0$ | 45.6 | 52.7 | 84.3 |
| $\overrightarrow{\xi_{3}}$ of H6 | 46.2 | $0 / 0$ | 88.2 | 71.0 |
| $\overrightarrow{\xi_{3}}$ of H7 | 48.6 | 86.3 | $0 / 0$ | 73.9 |
| $\overrightarrow{\xi_{3}}$ of H8 | 87.0 | 73.0 | 71.1 | $0 / 0$ |

Table SI9. Angles (in degrees) between the eigenvectors associated with the most shielded eigenvalue of $\{\mathrm{H} 5, \mathrm{H} 6, \mathrm{H} 7, \mathrm{H} 8\}$ protons and the corresponding $\mathrm{O}-\mathrm{H}$ bond vector in citric acid discussed in the main text (the GIAO-B3LYP/6-311++G(2d,2p) results were obtained for the cluster model, the GIPAW-PBE for the periodic structure).

| site, $k$ | angle between $\overrightarrow{\|O k-\mathrm{H} k\|}$ and $\overrightarrow{\xi_{3}}$ of $\mathrm{H} k$ |  |
| :---: | :---: | :---: |
|  | GIPAW-PBE | B3LYP-GIAO |
| 5 | 12.4 | 10.8 |
| 6 | 19.8 | 15.4 |
| 7 | 19.9 | 23.7 |
| 8 | 16.6 | 13.2 |

Table SI10. The scan of the ${ }^{1} \mathrm{H}$ NMR parameters of the phenolic proton in the phenol-water dimer described in the main text (both the GIAO-B3LYP and GIAO-MP2 calculations were performed with the $6-311++G(2 d, 2 p)$ basis set for the MP2/aug-cc-pVTZ geometry).

| distance <br> between the <br> oxygens (in <br> picometers) | angle (in radians) between $\overrightarrow{\xi_{3}}$ and <br> the line connecting the oxygens |  | $\sigma^{\text {iso }}$ (in ppm) |  |
| :---: | :---: | :---: | :---: | :---: |
|  | 0.1407 | 0.1392 | 21.7608 | 21.7245 |
| 265.5 | 0.1429 | 0.1412 | 22.2620 | 22.2250 |
| 270.0 | 0.1452 | 0.1432 | 22.7143 | 22.6754 |
| 274.5 | 0.1474 | 0.1451 | 23.1222 | 23.0803 |
| 279.0 | 0.1496 | 0.1470 | 23.4890 | 23.4434 |
| 283.5 | 0.1518 | 0.1488 | 23.8209 | 23.7711 |
| 288.0 | 0.1539 | 0.1505 | 24.1205 | 24.0661 |
| 292.5 | 0.1560 | 0.1523 | 24.3910 | 24.3317 |
| 297.0 | 0.1580 | 0.1539 | 24.6355 | 24.5709 |
| 301.5 | 0.1600 | 0.1555 | 24.8573 | 24.7873 |
| 306.0 | 0.1619 | 0.1570 | 25.0581 | 24.9828 |
| 310.5 | 0.1638 | 0.1584 | 25.2391 | 25.1590 |
| 315.0 | 0.1656 | 0.1598 | 25.4039 | 25.3190 |
| 319.5 | 0.1674 | 0.1612 | 25.5538 | 25.4639 |
| 324.0 | 0.1691 | 0.1625 | 25.6908 | 25.5951 |
| 328.5 | 0.1707 | 0.1637 | 25.8160 | 25.7139 |
| 333.0 | 0.1723 | 0.1649 | 25.9313 | 25.8220 |
| 337.5 | 0.1738 | 0.1660 | 26.0367 | 25.9203 |
| 342.0 | 0.1753 | 0.1671 | 26.1327 | 26.0098 |
| 346.5 | 0.1767 | 0.1681 | 26.2201 | 26.0912 |
| 351.0 | 0.1781 | 0.1691 | 26.3002 | 26.1659 |

For the calculated ${ }^{1} \mathrm{H}$ CST of the H 1 site of malonic acid, with the eigenvalues $\sigma_{11}, \sigma_{22}, \sigma_{33}\left(\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}\right)$ and their associated eigenvectors $\overrightarrow{\chi_{1}}, \overrightarrow{\chi_{2}}, \overrightarrow{\chi_{3}}$, it is convenient to employ the reference frame given by the vectors $\vec{p}, \vec{q}, \vec{r}$ that are defined as follows: $\vec{p}$ is a normal vector to the $\mathrm{O} 1-\mathrm{C} 2-\mathrm{O} 2$ plane; $\vec{q}$ is a vector which is perpendicular to the $\mathrm{O} 1-\mathrm{H} 1$ bond vector and which lies in the $\mathrm{O} 1-\mathrm{C} 2-\mathrm{O} 2$ plane; $\vec{r}$ is a vector parallel to the $\mathrm{O} 1-\mathrm{H} 1$ bond vector. The angles between the respective vectors from $\left\{\overrightarrow{\chi_{1}}, \overrightarrow{\chi_{2}}, \overrightarrow{\chi_{3}}\right\}$ and $\{\vec{p}, \vec{q}, \vec{r}\}$ sets are given by $A=\cos ^{-1} B$; using the shorthand notation $(a, b)$ for the absolute value of the scalar product of the vectors $\vec{a}$ and $\vec{b}:|\vec{a} \cdot \vec{b}|$, the matrix $B$ is

$$
B=\left[\begin{array}{lll}
\left(\chi_{1}, p\right) & \left(\chi_{2}, p\right) & \left(\chi_{3}, p\right) \\
\left(\chi_{1}, q\right) & \left(\chi_{2}, q\right) & \left(\chi_{3}, q\right) \\
\left(\chi_{1}, r\right) & \left(\chi_{2}, r\right) & \left(\chi_{3}, r\right)
\end{array}\right]
$$

For the PW-PBE optimized structure with $\{\vec{p}, \vec{q}, \vec{r}\}$ :
$\begin{array}{lll}0.9975 & 0.0560 & 0.0425\end{array}$
$-0.0203 \quad 0.8079-0.5889$
$-0.1482 \quad 0.5801 \quad 0.8009$
and with the GIPAW-PBE $\left\{\overrightarrow{\chi_{1}}, \overrightarrow{\chi_{2}}, \overrightarrow{\chi_{3}}\right\}$ :
$0.9830 \quad 0.0948 \quad 0.1570$
$-0.0162 \quad 0.8975$-0.4406
$-0.1827 \quad 0.4306 \quad 0.8838$
the elements of the matrix $A$ are (in degrees):
$\begin{array}{lll}7 & 89 & 83\end{array}$
$88 \quad 10 \quad 80$
$88 \quad 80 \quad 10$
This means $\overrightarrow{\chi_{1}}$ is approximately perpendicular to the O1-C2-O2 plane, $\overrightarrow{\chi_{2}}$ is approximately perpendicular to the $\mathrm{O} 1-\mathrm{H} 1$ bond, and $\overrightarrow{\chi_{3}}$ is almost collinear with the $\mathrm{O} 1-\mathrm{H} 1$ bond.


For the calculated ${ }^{1} \mathrm{H}$ CST of the H 2 site of malonic acid, with the eigenvalues $\sigma_{11}, \sigma_{22}, \sigma_{33}\left(\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}\right)$ and their associated eigenvectors $\overrightarrow{\chi_{1}}, \overrightarrow{\chi_{2}}, \overrightarrow{\chi_{3}}$, it is convenient to employ the reference frame given by the vectors $\vec{p}, \vec{q}, \vec{r}$ that are defined as follows: $\vec{p}$ is a normal vector to the $\mathrm{O} 3-\mathrm{C} 3-\mathrm{O} 4$ plane; $\vec{q}$ is a vector which is perpendicular to the $\mathrm{O} 4-\mathrm{H} 2$ bond vector and which lies in the $\mathrm{O} 3-\mathrm{C} 3-\mathrm{O} 4$ plane; $\vec{r}$ is a vector parallel to the $\mathrm{O} 4-\mathrm{H} 2$ bond vector. The angles between the respective vectors from $\left\{\overrightarrow{\chi_{1}}, \overrightarrow{\chi_{2}}, \overrightarrow{\chi_{3}}\right\}$ and $\{\vec{p}, \vec{q}, \vec{r}\}$ sets are given by $A=\cos ^{-1} B$; using the shorthand notation $(a, b)$ for the absolute value of the scalar product of the vectors $\vec{a}$ and $\vec{b}:|\vec{a} \cdot \vec{b}|$, the matrix $B$ is

$$
B=\left[\begin{array}{lll}
\left(\chi_{1}, p\right) & \left(\chi_{2}, p\right) & \left(\chi_{3}, p\right) \\
\left(\chi_{1}, q\right) & \left(\chi_{2}, q\right) & \left(\chi_{3}, q\right) \\
\left(\chi_{1}, r\right) & \left(\chi_{2}, r\right) & \left(\chi_{3}, r\right)
\end{array}\right]
$$

For the PW-PBE optimized structure with $\{\vec{p}, \vec{q}, \vec{r}\}$ :
$-0.1558 \quad 0.8232 \quad 0.5460$
$0.9870 \quad 0.1516 \quad 0.0530$
$-0.0476 \quad 0.5914 \quad-0.8050$
and with the GIPAW-PBE $\left\{\overrightarrow{\chi_{1}}, \overrightarrow{\chi_{2}}, \overrightarrow{\chi_{3}}\right\}$ :
$-0.1709 \quad 0.7812 \quad 0.6005$
$0.9613 \quad 0.2658-0.0723$
$\begin{array}{lll}0.2161 & -0.5649 & 0.7964\end{array}$
the elements of the matrix $A$ are (in degrees):
$4 \quad 88 \quad 86$
$89 \quad 10 \quad 80$
$89 \quad 80 \quad 10$
This means $\overrightarrow{\chi_{1}}$ is approximately perpendicular to the O3-C3-O4 plane, $\overrightarrow{\chi_{2}}$ is approximately perpendicular to the $\mathrm{O} 4-\mathrm{H} 2$ bond, and $\overrightarrow{\chi_{3}}$ is almost collinear with the $\mathrm{O} 4-\mathrm{H} 2$ bond.


For the calculated ${ }^{1} \mathrm{H}$ CST of the H 3 site of malonic acid, with the eigenvalues $\sigma_{11}, \sigma_{22}, \sigma_{33}\left(\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}\right)$ and their associated eigenvectors $\overrightarrow{\chi_{1}}, \overrightarrow{\chi_{2}}, \overrightarrow{\chi_{3}}$, it is convenient to employ the reference frame given by the vectors $\vec{p}, \vec{q}, \vec{r}$ that are defined as follows: $\vec{p}$ is a normal vector to the $\mathrm{H} 3-\mathrm{C} 1-\mathrm{C} 3$ plane; $\vec{q}$ is a vector which is perpendicular to the $\mathrm{C} 1-\mathrm{H} 3$ bond vector and which lies in the $\mathrm{H} 3-\mathrm{C} 1-\mathrm{C} 3$ plane; $\vec{r}$ is a vector parallel to the $\mathrm{C} 1-\mathrm{H} 3$ bond vector. The angles between the respective vectors from $\left\{\overrightarrow{\chi_{1}}, \overrightarrow{\chi_{2}}, \overrightarrow{\chi_{3}}\right\}$ and $\{\vec{p}, \vec{q}, \vec{r}\}$ sets are given by $A=\cos ^{-1} B$; using the shorthand notation $(a, b)$ for the absolute value of the scalar product of the vectors $\vec{a}$ and $\vec{b}:|\vec{a} \cdot \vec{b}|$, the matrix $B$ is

$$
B=\left[\begin{array}{lll}
\left(\chi_{1}, p\right) & \left(\chi_{2}, p\right) & \left(\chi_{3}, p\right) \\
\left(\chi_{1}, q\right) & \left(\chi_{2}, q\right) & \left(\chi_{3}, q\right) \\
\left(\chi_{1}, r\right) & \left(\chi_{2}, r\right) & \left(\chi_{3}, r\right)
\end{array}\right]
$$

For the PW-PBE optimized structure with $\{\vec{p}, \vec{q}, \vec{r}\}$ :
$-0.3769-0.8065-0.4555$
$0.2058 \quad 0.4066-0.8901$
$\begin{array}{lll}0.9031 & -0.4293 & 0.0127\end{array}$
and with the GIPAW-PBE $\left\{\overrightarrow{\chi_{1}}, \overrightarrow{\chi_{2}}, \overrightarrow{\chi_{3}}\right\}$ :
$\begin{array}{lll}0.4276 & 0.6609 & 0.6168\end{array}$
$0.4498 \quad 0.4363-0.7793$
$-0.7841 \quad 0.6106-0.1107$
the elements of the matrix $A$ are (in degrees):
$13 \quad 80 \quad 82$
$\begin{array}{lll}79 & 15 & 79\end{array}$
$84 \quad 78 \quad 14$
This means $\overrightarrow{\chi_{1}}$ is approximately perpendicular to the $\mathrm{H} 3-\mathrm{C} 1-\mathrm{C} 3$ plane, $\overrightarrow{\chi_{2}}$ is approximately perpendicular to the $\mathrm{C} 1-\mathrm{H} 3$ bond, and $\overrightarrow{\chi_{3}}$ is almost collinear with the $\mathrm{C} 1-\mathrm{H} 3$ bond.


For the calculated ${ }^{1} \mathrm{H}$ CST of the H 4 site of malonic acid, with the eigenvalues $\sigma_{11}, \sigma_{22}, \sigma_{33}\left(\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}\right)$ and their associated eigenvectors $\overrightarrow{\chi_{1}}, \overrightarrow{\chi_{2}}, \overrightarrow{\chi_{3}}$, it is convenient to employ the reference frame given by the vectors $\vec{p}, \vec{q}, \vec{r}$ that are defined as follows: $\vec{p}$ is a normal vector to the $\mathrm{H} 4-\mathrm{C} 1-\mathrm{C} 3$ plane; $\vec{q}$ is a vector which is perpendicular to the $\mathrm{C} 1-\mathrm{H} 4$ bond vector and which lies in the $\mathrm{H} 4-\mathrm{C} 1-\mathrm{C} 3$ plane; $\vec{r}$ is a vector parallel to the $\mathrm{C} 1-\mathrm{H} 4$ bond vector. The angles between the respective vectors from $\left\{\overrightarrow{\chi_{1}}, \overrightarrow{\chi_{2}}, \overrightarrow{\chi_{3}}\right\}$ and $\{\vec{p}, \vec{q}, \vec{r}\}$ sets are given by $A=\cos ^{-1} B$; using the shorthand notation $(a, b)$ for the absolute value of the scalar product of the vectors $\vec{a}$ and $\vec{b}:|\vec{a} \cdot \vec{b}|$, the matrix $B$ is

$$
B=\left[\begin{array}{lll}
\left(\chi_{1}, p\right) & \left(\chi_{2}, p\right) & \left(\chi_{3}, p\right) \\
\left(\chi_{1}, q\right) & \left(\chi_{2}, q\right) & \left(\chi_{3}, q\right) \\
\left(\chi_{1}, r\right) & \left(\chi_{2}, r\right) & \left(\chi_{3}, r\right)
\end{array}\right]
$$

For the PW-PBE optimized structure with $\{\vec{p}, \vec{q}, \vec{r}\}$ :
$-0.6028 \quad 0.6365 \quad 0.4811$
$-0.3966 \quad 0.2842 \quad-0.8729$
$-0.6924 \quad-0.7170 \quad 0.0811$
and with the GIPAW-PBE $\left\{\overrightarrow{\chi_{1}}, \overrightarrow{\chi_{2}}, \overrightarrow{\chi_{3}}\right\}$ :
$\begin{array}{lll}0.7851 & -0.5673 & -0.2485\end{array}$
$0.3229 \quad 0.0326 \quad 0.9459$
$-0.5285-0.82290 .2088$
the elements of the matrix $A$ are (in degrees):
$\begin{array}{lll}17 & 74 & 84\end{array}$
$\begin{array}{lll}75 & 19 & 78\end{array}$
$81 \quad 80 \quad 13$
This means $\overrightarrow{\chi_{1}}$ is approximately perpendicular to the $\mathrm{H} 4-\mathrm{C} 1-\mathrm{C} 3$ plane, $\overrightarrow{\chi_{2}}$ is approximately perpendicular to the $\mathrm{C} 1-\mathrm{H} 4$ bond, and $\overrightarrow{\chi_{3}}$ is almost collinear with the $\mathrm{C} 1-\mathrm{H} 4$ bond.


