PHYSICAL REVIEW B **71**, 115110 (2005)

Core spin-polarization correction in pseudopotential-based electronic structure calculations

Oleg V. Yazyev,* Ivano Tavernelli, Lothar Helm, and Ursula Röthlisberger
École Polytechnique Fédérale de Lausanne, Institut des Sciences et Ingénierie Chimiques, EPFL-BCH,
CH-1015 Lausanne, Switzerland

(Received 8 September 2004; revised manuscript received 11 November 2004; published 16 March 2005)

A simple scheme for the evaluation of the core spin-polarization contribution within pseudopotential electronic structure methods is proposed. The method uses a reconstruction of the all-electron wave functions and the frozen valence spin-density approximation to solve the Kohn-Sham equations for core electrons only. The core contribution to the spin-density at the point of the nucleus corrects for the leading error in the Fermi contact hyperfine coupling constants within pseudopotential-based electronic structure calculations. The correction is implemented in the framework of pseudopotential plane-wave density functional theory. Comparison with all-electron Slater-type orbital calculations on a number of molecular radicals containing first-row elements proves the accuracy of this approach.

DOI: 10.1103/PhysRevB.71.115110 PACS number(s): 31.15.Ew, 31.30.Gs, 32.10.Fn, 33.15.Pw

Magnetic resonance methods are powerful tools for the experimental investigation of structural and dynamic properties in molecular and condensed matter systems. Electronic structure theory, especially density functional theory (DFT) methods, became very popular for modeling and understanding results from magnetic resonance experiments.[1] One of the most important parameters in electron paramagnetic resonance (EPR) and nuclear magnetic resonance (NMR) experiments on paramagnetic systems is the isotropic (Fermi contact) hyperfine coupling constant, which describes the magnetic interaction between the nuclear and electronic spins under isotropic averaging conditions. This property is related to electron spin-density $\rho^s(r)=\rho^{\uparrow}(r)-\rho^{\downarrow}(r)$ at the point of nucleus I, r_I, in a very simple way:

$$A_{iso}(I)=\frac{4\pi}{3}\mu_e\mu_N g_e g_I\langle S_z\rangle^{-1}\rho^s(r_I), \tag{1}$$

where μ_e and μ_I are Bohr and nuclear magnetons, g_e and g_I are g-values of free electron and nucleus I, respectively, and $\langle S_z\rangle$ is the expectation value of the total electronic spin z-component.

In spite of its apparent simplicity, the local nature of this property makes its computation difficult for electronic structure theory methods based on the optimization of global properties such as the total energy. While all-electron (AE) approaches based on localized basis sets (e.g., Gaussian or Slater-type atomic orbitals (STO)) have already proven to give satisfactory results for the calculation of isotropic hyperfine coupling constants, there is still a lack of methods for its calculation in pseudopotential-based approaches. These are of particular importance for condensed matter physics[2] and plane-wave- (PW) based first-principles dynamics applications in chemistry and biology.[3]

The difficulty in evaluating the electron spin-density at the point of the nucleus within pseudopotential-based calculations is due to two main sources. The first one concerns the behavior of the pseudo wave functions in the vicinity of the nucleus (within the predefined core radius) which differ from the AE ones while playing a decisive role in the determination of the isotropic hyperfine coupling constants. The simplest solution to this problem was proposed by Van de Walle and Blöchl.[4] However, this correction does not solve the problem of the behavior of the exchange-correlation potential in the vicinity of the nucleus, necessary for a correct description of spin-polarization effects on the valence orbitals. Furthermore, no extended benchmarks of this method were provided until now. Secondly, the complete elimination of the core electrons in pseudopotential calculations implies the complete disregard of the core spin-polarization contribution to the Fermi contact hyperfine coupling constants. While this effect has only a negligible influence on the valence wave functions of the system, its contribution to the isotropic hyperfine coupling constants can be significant. This is explained by the high magnitudes of the atomic s-type wave functions at the point of the nucleus, which in turn can result in a high value of the spin density.

Here, we will consider the spin density at the point of the nucleus $\rho^s(r_I)$ as the sum of the respective valence and core contributions, $\rho_v^s(r_I)$ and $\rho_c^s(r_I)$. It is worth mentioning that in AE approaches these contributions can be estimated by means of calculations based on the frozen core approximation or by analysis of the orbital contributions to the spin density. Some illustrative examples of such analyses from Ref. 5 prove that in most cases, core spin-polarization cannot be neglected. This is, for instance, the case when the unpaired spin populates other than s-type atomic orbitals centered on the considered atom.

Here, we present a simple approach for the estimation of the core spin-polarization contribution to the total spin density. It is based on the solution of the unrestricted Kohn-Sham equations for core states only in the external potential of frozen valence (FV) spin-up and spin-down electron densities (termed FV spin-density below). These densities are constructed in order to reproduce those of the molecular system under consideration in the core region of the nucleus I. In practice, this can be achieved using both basis-set-based approaches or numerical calculations on a spherically symmetric atom. While the first approach depends substantially on the choice of a basis set, making it less flexible, the sec-

TABLE I. $\rho_c^s(0)$ (in a.u.$^{-3}$) from AE and FV spin-density numerical atomic calculations using the exchange-correlation density functional of Perdew, Burke and Ernzenhof.[8]

Atom	Configuration	$\rho_c^s(0)$, AE	$\rho_c^s(0)$, FV
C	$2s\{1\uparrow,1\downarrow\}2p\{2\uparrow,0\downarrow\}$	−0.199294	−0.199265
N	$2s\{1\uparrow,1\downarrow\}2p\{3\uparrow,0\downarrow\}$	−0.441030	−0.440956
O	$2s\{1\uparrow,1\downarrow\}2p\{3\uparrow,1\downarrow\}$	−0.417946	−0.417854
F	$2s\{1\uparrow,1\downarrow\}2p\{3\uparrow,2\downarrow\}$	−0.273401	−0.273335

ond one implies that for the calculation of the property of interest, the error introduced by the spherical averaging of the external potential can be neglected.

Our implementation is based on the second method. A very similar approach was proposed by Vackář *et al.* for construction of "all-electron" pseudopotentials,[6,7] which take into account the response of the effective core potential to the changes in the valence wave functions. The accuracy of a frozen valence spin-density approach for the calculation of $\rho_c^s(r_I)$ can be validated in the case of atoms ($r_I=0$ for simplicity) using the following simple computational scheme. Here we limit our study to the first-row atoms C, N, O, and F using electronic configurations where only the p-shell is spin-polarized. For the first-row atoms, the core electrons belong only to the 1s shell, thus, the core contribution to the spin density at the point of the atomic nucleus can be written as $\rho_c^s(0)=\phi_{1s}^{\uparrow 2}(0)-\phi_{1s}^{\downarrow 2}(0)$. The densities $\rho_v^{\uparrow}(r)$ and $\rho_v^{\downarrow}(r)$ are obtained from FC calculations, where the atomic core wave functions $\phi_{1s}^{\uparrow}(r)=\phi_{1s}^{\downarrow}(r)$ are taken from AE calculations in the corresponding spin-averaged configuration $2s\{1\uparrow,1\downarrow\}2p\{(n/2)\uparrow,(n/2)\downarrow\}$. The results of our FV spin-density calculations based on the above mentioned $\rho_v^{\uparrow}(r)$ and $\rho_v^{\downarrow}(r)$ are then compared with AE results for $\rho_c^s(0)$ (See Table I). For light atoms, we observed that the difference between these two approaches never exceeds 0.1%. Thus, the core spin-polarization has almost no influence on the valence wave functions of these atoms. It should also be mentioned that in the case of first-row atoms with a spin-polarized p shell, $\rho_v^s(0)$ is positive and of comparable magnitude to the core contribution. Therefore, the neglect of core spin-polarization may results in large errors in the Fermi contact hyperfine coupling constants. Figure 1 illustrates the spin-polarization for nitrogen atom in its quartet spin-state ($2s\{1\uparrow,1\downarrow\}2p\{3\uparrow,0\downarrow\}$ configuration). In this case the spin density at $r=0$ is the result of the spin-polarization of the states 1s and 2s due to the different exchange-correlation potentials for spin-up and spin-down electrons. We observe that $\rho_c^s(0)$ $[=\rho_{1s}^s(0)]$ and $\rho_v^s(0)$ $[=\rho_{2s}^s(0)]$ are comparable in their magnitude while their signs differ: the core spin-density has a negative value in contrast to the valence one. Both contributions have sharp extrema at the point of nucleus, but integrate to zero. Similar behavior was observed for the series of benchmark molecules chosen as validation examples.

The electronic structure calculations of more complicated molecular and condensed matter systems using pseudopotentials require some additional care. In this case a reconstruction of the AE wave functions[9,4,10] $\psi_i^{\uparrow(\downarrow)}(r)$ from the pseudo wave functions $\tilde{\psi}_i^{\uparrow(\downarrow)}(r)$ has to be performed since the shapes of $\tilde{\psi}_i^{\uparrow(\downarrow)}(r)$ differ from those of $\psi_i^{\uparrow(\downarrow)}(r)$ within the core radius r_c around the nucleus. A variety of different techniques have been proposed for this purpose (see, e.g., the schemes proposed in Ref. 10). Here, we propose an even simpler procedure that takes into account the specificity of our problem. In our approach, we construct an atom in which spin-up and spin-down valence electron densities $\rho_v^{\uparrow(\downarrow)}(r)$ mimic those of the system under consideration in the neighborhood of the nucleus I. We expand these densities in terms of the spin-up and spin-down partial atomic occupation numbers $\omega_l^{\uparrow(\downarrow)}$ and the valence orbitals $\phi_l(r)$ of the AE atom (all orbitals correspond to the same spin-averaged AE wave functions, used to generate the pseudopotentials):

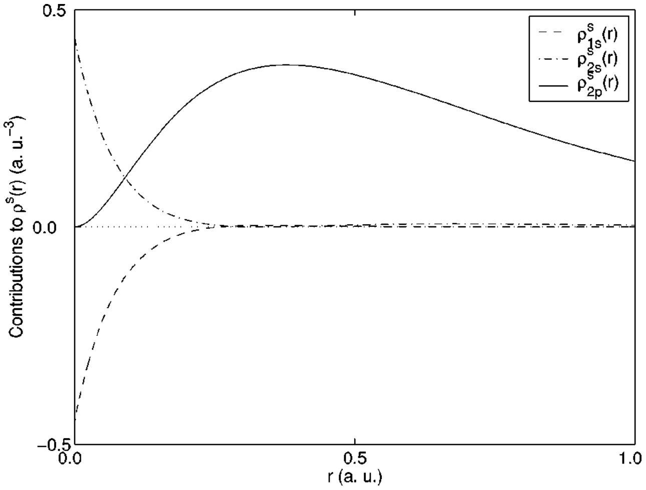

FIG. 1. The contributions to the $\rho^s(r)$ in spin-polarized nitrogen atom.

$$\rho_v^{\uparrow(\downarrow)}(r)=\sum_l \omega_l^{\uparrow(\downarrow)}\phi_l^2(r). \tag{2}$$

The occupation numbers can be calculated using the following general expression:

$$\omega_l^{\uparrow(\downarrow)}=\sum_i^{N_{\uparrow(\downarrow)}}\sum_{m=-l}^{l}\langle\tilde{\psi}_i^{\uparrow(\downarrow)}(r)|\tilde{\phi}_{lm}(r)\rangle_{r_c}\langle\tilde{\phi}_{lm}(r)|\tilde{\psi}_i^{\uparrow(\downarrow)}(r)\rangle_{r_c}, \tag{3}$$

assuming that the pseudo atomic orbitals form a complete basis set within a small radius r_c around the nucleus. The notation $\langle\cdot|\cdot\rangle_{r_c}$ stands for the "localized" overlap within the radius r_c around the nucleus. The pseudo atom valence orbitals $\tilde{\phi}_{lm}(r)=\tilde{R}_l(r)Y_{lm}(r)$ are represented as the product of the radial part $\tilde{R}_l(r)$ and the spherical harmonic $Y_{lm}(r)$. $N^{\uparrow}$ and $N^{\downarrow}$ are the numbers of spin-up and spin-down electrons in the system, correspondingly. For periodic systems, the proper sampling of the first Brillouin zone must also be included in these expressions to take into account for the dependence of the pseudo wave functions of the system on the crystal momentum. This approach is equivalent to that proposed by Vackář *et al.* for the reconstruction of the part of the spherically averaged valence atomic electron density at $r\leqslant R_C$ [Eq. (8) in Ref. 7].

TABLE II. Fermi contact hyperfine coupling constants (in Gauss units) in seven molecular radicals. The values correspond to pseudopotential plane-wave approach (PP PW), same method corrected for core spin-polarization of first-row atoms (PP PW+CSPC), frozen core calculations using STO basis set (FC STO), all-electron STO calculations (AE STO), and experimental values.

		A_{iso}				
Molecule	Nucleus	PP PW	PP PW + CSPC	FC STO	AE STO	Exp.[a]
CH_3	^1H	−23.3		−25.3	−25.3	−25.1[b];−23.04[c]
	^{13}C	66.4	26.5	60.9	30.2	28.4[b];38.34[c]
C_2H_3	$^1H^{\alpha}$	15.6		15.1	15.0	12.8
	$^1H_a^{\beta}$	64.9		68.4	68.4	65.9
	$^1H_s^{\beta}$	40.6		43.6	43.5	39.6
	$^{13}C^{\alpha}$	−8.3	−4.1	−9.0	−5.2	−8.6
	$^{13}C^{\beta}$	141.0	106.0	131.1	107.4	107.6
C_3H_5	$^1H^{\alpha}$	3.8		3.6	3.6	4.1
	$^1H^{\beta 1}$	−15.0		−15.2	−15.2	−14.8
	$^1H^{\beta 2}$	−13.9		−14.3	−14.3	−13.9
	$^{13}C^{\alpha}$	−21.9	−14.6	−19.8	−15.5	−17.2
	$^{13}C^{\beta}$	41.3	17.0	36.3	17.3	21.9
H_2CN	^1H	85.2		89.0	89.0	83.2
	^{13}C	−26.9	−22.1	−26.2	−23.3	−28.9
	^{14}N	21.1	4.2	18.8	5.6	9.3
HCO	^1H	133.8		136.1	136.0	135.4
	^{13}C	162.0	146.7	151.4	139.1	133.9
	^{17}O	−23.0	−9.5	−18.8	−10.3	−15.1
FCO	^{19}F	405.5	346.9	368.3	276.3	323.2
	^{13}C	303.9	293.6	285.6	280.1	286.6
	^{17}O	−25.5	−16.6	−21.7	−16.1	
NO_2	^{14}N	62.1	57.3	60.9	52.2	54.8
	^{17}O	−32.8	−18.5	−26.0	−17.6	−16.3 – −20.3

[a] References 21–23.

[b] Experimental results for a hypothetical nonvibrating molecule from Ref. 21.

[c] Direct experimental results from Ref. 22.

Our implementation is based on the following expression for the atomic occupation numbers

$$\omega_l^{\uparrow(\downarrow)} = \sum_{i}^{N_{\uparrow(\downarrow)}} \sum_{m=-l}^{l} \frac{\langle f(r) Y_{lm}(r) | \tilde{\psi}_i^{\uparrow(\downarrow)}(r) \rangle^2}{\langle f(r) | \tilde{R}_l(r) \rangle^2}, \tag{4}$$

where the cutoff function $f(r)$ is used in order to limit the overlap integral only to the region localized around the nucleus under consideration. A similar methodology was used by Van de Walle and Blöchl in their derivation of the expression for the anisotropic hyperfine parameters.[4] For reasons of computation efficiency in our implementation expression (4) is evaluated in Fourier space. We take a cutoff function $f(G)=1$, which in the real space representation approaches a Dirac delta function $\delta(r=0)$ when the PW kinetic energy cutoff tends to infinity: $E_{kin} \rightarrow \infty$. Another motivation for this choice is that in this case $\omega_0^{\uparrow(\downarrow)} = \tilde{\rho}_v^{\uparrow(\downarrow)}(0) / \tilde{R}_0^2(0)$, and therefore one obtains $\rho_v^s(0) = (\omega_0^{\uparrow} - \omega_0^{\downarrow}) \phi_0^2(0) = \tilde{\rho}_v^s(0) R_0{}^2(0) / \tilde{R}_0^2(0)$, which is identical to the "scaling up the spin density" formula from Ref. 4. Other definitions of the cutoff function $f(r)$ are also possible, but we do not discuss them further in this article.

To provide the necessary benchmarks, we compare the quality of our results based on pseupotentials and PW basis sets with AE calculations performed using Slater-type orbitals. STO basis sets correctly describe the cusp condition and thus usually provide the most accurate theoretical predictions of hyperfine coupling constants. The benchmark set consists of a representative series of small molecular doublet radicals containing only hydrogen and first-row atoms C, N, O, and F (the core spin-polarization effects are important for these atoms and originate uniquely from the 1*s* core shell). For these molecules reliable experimental data are also available together with computational results obtained from both AE DFT and high level *ab initio* methods. For the sake of completeness, we also compare our results for pseudopotential PW calculations with FC AE calculations in order to estimate the importance of core spin-polarization effects. The results are given in Table II.

The basic target of this work is not an accurate reproduc-

TABLE III. Cutoff radii r_c used for the pseudopotential generation and NLCC core radii r_{core} (in a.u.). The same values of r_c were used for both s and p channels of first-row elements.

	H	C	N	O	F
r_c	0.5	1.14	0.96	0.83	0.73
r_{core}	⋯	1.03	0.77	0.65	0.58

tion of experimental data, but rather a comparison of two different computational methodologies in the context of what is known experimentally. For this reason, vibrational averaging or environment effects, important for the precise prediction of hyperfine coupling constants were not taken into account. In both approaches, we use the Becke gradient-corrected exchange density functional[11] together with the correlation gradient-corrected density functional proposed by Perdew.[12] The unrestricted solution of the Kohn-Sham equations was used in order to account for spin-polarization effects in the valence wave functions. In the PW calculations, we used original norm-conserving Troullier-Martins[13] (TM) pseudopotentials generated from spin-averaged wave functions computed for atoms in their ground states. For the construction of the hydrogen atom pseudopotential, we used an occupation number of 0.7 instead of the nominal value 1.0. The cutoff radii used in the generation of all other pseudopotentials are the same as the ones given in Ref. 14. These values correspond to rather hard pseudopotentials. Nonlinear core corrections[15] (NLCC) were applied for the first-row elements. The NLCC core radii were chosen experimentally to achieve a compromise between a reasonable NLCC "softness" and accuracy of results. For clarity, all these values are summarized in Table III.

The Gauss-Hermite integration with 16 points was used for the calculation of the nonlocal parts of the pseudopotential. The calculations were performed in $12\times12\times12$ Å^3 isolated cubic box using Tuckerman-Martyna's Poisson equation solver.[16] The size of the box was chosen large enough to make the results consistent with STO calculations on isolated molecules. The PW cutoff of 100 Ry for the wave function expansion was chosen to ensure the basis set completeness,[17] while for the electron density expansion a consistent cutoff of 400 Ry was used. The first Brillouin zone was sampled only at the Γ point. These calculations were performed with a modified version of the CPMD code.[18] STO calculations were performed with the basis set of triple-zeta plus double polarization (TZ2P) quality using the ADF2004 code.[19] All geometries were optimized at the same level of theory using STO basis sets. We use FV spin-density calculations implemented in a numerical atomic DFT code[20] that allows for predefined frozen wave functions and partial atomic occupation numbers. The AE wave functions were reconstructed taking into account only the s-channel for H, while for the first-row atoms the p-channel was also reconstructed. This is a necessary condition for an accurate evaluation of the correction since spin population of valence p-type orbitals often produce a strong spin-polarization of s-core orbitals (See Chap. 29 in Ref. 1).

The results in Table II prove the accuracy of the proposed correction scheme. For the simplest case of ^{1}H hyperfine coupling constants, no spin-polarization effects occur and the pseudo wave functions in the vicinity of these nuclei resemble the AE wave functions apart from the absence of the nuclear cusps. Thus, the wave function reconstruction approach proposed by Van de Walle and Blöchl gives results very close to the AE STO calculations and to experimental data as well. Comparison between the AE calculations and the FC STO calculations also shows small differences in the ^{1}H hyperfine coupling constants. This confirms the hypothesis about the negligible influence of the spin polarization of core orbitals on the valence ones. For heavier elements in the first row of the periodic table the core spin-polarization contribution is present. From Table II one can see that $\rho_c^s(r_I)$ is usually lower in magnitude and has an opposite sign compared to $\rho_v^s(r_I)$. In some cases $\rho_c^s(r_I)$ is negligible, while in others (e.g., ^{14}N hyperfine coupling constant in H_2CN) it cannot be neglected. This observation is in perfect agreement with the STO calculations. In addition, the systematic overestimation of the value of $\rho_v^s(r_I)$, which increases along the first-row elements series moving from carbon to fluorine, is observed. This discrepancy is related to the difference between exchange-correlation potentials for spin-up and spin-down electrons within the core region of the atoms. This difference is poorly represented in pseudopotential calculations compared to AE ones because of the smooth behavior of pseudo wave functions. Moreover, this effect tends to become larger moving towards the heavier elements of the series.

In conclusion, the proposed core spin-polarization correction recovers the largest part of the error in pseudopotential PW calculations when compared to AE calculations and experimental results. Hopefully, ongoing developments in the design of new pseudopotentials and wave function reconstruction techniques together with the use of frozen valence spin-density calculations will reduce this gap even further.

ACKNOWLEDGMENTS

We acknowledge support from the Swiss National Science Foundation. Authors also thank Alfredo Pasquarello for discussion and José Luís Martins for the kind permission to use and adapt to our needs the atomic code he is now maintaining. The computational resources were provided by the Swiss Center for Scientific Computing and the DIT-EPFL.

*Electronic address: oleg.yazyev@epfl.ch

[1] *Calculation of NMR and EPR parameters: Theory and Applications*, edited by M. Kaupp, M. Bühl, and V. G. Malkin (Wiley-VCH, Weinheim, 2004).

[2] W. E. Pickett, Comput. Phys. Rep. **9**, 115 (1989).

[3] W. Andreoni and A. Curioni, Parallel Comput. **26**, 819 (2000).

[4] C. G. Van de Walle and P. E. Blöchl, Phys. Rev. B **47**, 4244 (1993).

[5] M. L. Munzarová, P. Kubáček, and M. Kaupp, J. Am. Chem. Soc. **122**, 11900 (2000).

[6] J. Vackář and A. Šimůnek, J. Phys.: Condens. Matter **6**, 3025 (1994). J. Vackář, A. Šimůnek, and R. Podloucky, Phys. Rev. B **53**, 7727 (1996).

[7] J. Vackář, M. Hyt'ha, and A. Šimůnek, Phys. Rev. B **58**, 12 712 (1998).

[8] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[9] B. Hetényi, F. D. Angelis, P. Giannozzi, and R. Car, J. Chem. Phys. **115**, 5791 (2001).

[10] B. Meyer, K. Hummler, C. Elsässer, and M. Fähnle, J. Phys.: Condens. Matter **7**, 9201 (1995).

[11] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).

[12] J. P. Perdew, Phys. Rev. B **33**, 8822 (1986).

[13] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[14] D. Porezag, M. R. Pederson, and A. Y. Liu, Phys. Rev. B **60**, 14 132 (1999).

[15] S. G. Louie, S. Froyen, and M. L. Cohen, Phys. Rev. B **26**, 1738 (1982).

[16] G. J. Martyna and M. E. Tuckerman, J. Chem. Phys. **110**, 2810 (1999).

[17] The accuracy of the calculations with 100 Ry PW cutoff basis set was confirmed with 200 Ry cutoff calculations.

[18] CPMD version 3.9.1, Copyright IBM Corp 1990–2004, Copyright MPI für Festkörperforschung Stuttgart 1997–2001.

[19] G. te Velde, F. M. Bickelhaupt, S. J. A. van Gisbergen, C. F. Guerra, E. Baerends, J. G. Snijders, and T. Ziegler, J. Comput. Chem. **22**, 931 (2001); C. F. Guerra, J. G. Snijders, G. te Velde, and E. Baerends, Theor. Chem. Acc. **99**, 391 (1998); ADF2004.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com

[20] Two different spin-polarized DFT atomic codes were used. In the preliminary stage, we used the code originally written by Sverre Froyen, which is now part of the pseudopotential generation code maintained by José Luís Martins. The code is freely available at http://bohr.inesc-mn.pt/~jlm/pseudo.html. The other code is a modified version of the code maintained by Andrea Dal Corso, which is the part of the ESPRESSO program package. This package is distributed under the GNU GPL license and is freely available at http://www.democritos.it/scientific.php. Both codes give results that are in very close agreement.

[21] D. M. Chipman, Theor. Chim. Acta **82**, 93 (1992).

[22] E. Hirota and C. Yanada, J. Mol. Spectrosc. **96**, 175 (1985).

[23] R. W. Fessender and R. H. Schuler, J. Chem. Phys. **39**, 2147 (1963); R. W. Fessender, J. Phys. Chem. **71**, 74 (1967); H. J. McManus, R. W. Fessender, and D. M. Chipman, *ibid.* **92**, 3778 (1988); H. J. McManus, R. W. Fessender, and D. M. Chipman, *ibid.* **92**, 3781 (1988); F. J. Adrian, B. F. Kim, and J. Bohandy, J. Chem. Phys. **82**, 1804 (1985); F. J. Adrian, E. L. Cochran, and V. A. Bowers, *ibid.* **43**, 462 (1965); E. L. Cochran, F. J. Adrian, and V. A. Bowers, *ibid.* **44**, 4626 (1966); Z. Luz and A. Reuveni, *ibid.* **51**, 4017 (1969).