

Large local-field effects in the second-harmonic susceptibility of crystalline urea

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The linear-optical response and the nonlinear susceptibility for second-harmonic generation are calculated for crystalline urea within band theory using the Kohn-Sham local-density approximation, implemented with pseudopotentials and plane waves. In the low-frequency limit, the static dielectric constants are found to be 2.03 (ordinary) and 2.14 (extraordinary), vs 2.17 and 2.49, respectively, for the experimental values. For second-harmonic generation, Kleinmann symmetry is invoked to consider a single independent tensor component, $d_{14} = d_{36}$. The calculated value is 1.1 pm/V, compared to an experimental value of 1.2 ± 0.1 pm/V for d_{36} . Without local-field corrections, d would have been 2.1 pm/V. Hence, nonlinear local-field corrections are a key element of this calculation.

I. INTRODUCTION

Crystalline urea, formed with two formula units of $\text{CO}(\text{NH}_2)_2$ per unit cell, was among the first organic materials to find an application in nonlinear optics, specifically phase-matched second-harmonic generation (SHG) in the ultraviolet, as discussed in the review of Halbout and Tang.¹ The growth of urea crystals for application to optical parametric oscillators, frequency doubling, and frequency mixing remains a subject of current research interest.^{2,3} From a fundamental point of view, this crystal is interesting because it is among the simplest organic crystals which have a second-harmonic response.

The theoretical analysis of SHG for the crystal has been attempted, but it is difficult. The standard chemical theory of the second-harmonic susceptibility is the "oriented-gas" method with Lorentz local-field factors.⁴ This approximation has been used very recently in the analysis of the urea-derivative 5-nitroureicil.⁵ The assumption that the principal interactions are intramolecular breaks down for the case of urea which forms hydrogen bonds in the crystal.⁶ It has been recognized since the early days of nonlinear optics that the Lorentz local-field factors are not an appropriate correction for crystals with delocalized electrons.⁷

The standard approach of solid-state theory is to neglect local fields in the calculation of second-harmonic response. (In the previous sentence "local fields" are taken in the sense of Adler,⁸ Wiser,⁹ and Pine¹⁰ to represent a general spatially varying potential which acts in a distributed way throughout the unit cell of the material. This is in contrast to the Lorentz-type local-field correction, in which the material is assumed to be located at some particular point in space at which the effective field is given by the macroscopic field times a single constant factor.) Our earlier work^{11,12} has shown that second-harmonic local-field corrections are typically about 10%

for semiconductors, a figure which rises to 20% for trigonal selenium.¹³ Another group reports a 3% local-field correction in the case of GaAs.^{14,15}

Urea poses an interesting intermediate case: it is hydrogen bonded, which leads to enough delocalization to render the standard chemical approach inadequate, yet it has strong localized features such as π electrons in the carbonyl group which contribute significantly to the nonlinear response. The major result of this work is that our previously developed theory of second-harmonic generation including local fields remains adequate for urea, whereas the exclusion of these local fields would lead to a factor-of-2 discrepancy with experiment. Moreover, the standard approach of chemistry—based on noninteracting molecules—would be unlikely to succeed due to large intercell charge transfer.

The goal of the present study is to predict linear and nonlinear optical parameters of urea from a first-principles quantum-mechanical theory—specifically, band theory using the Kohn-Sham local-density approximation (LDA). The LDA has been used extensively for calculating a wide variety of material properties,¹⁶ including a recent survey of SHG in 15 III-V and II-VI semiconductors.¹⁷

II. THEORY AND CALCULATION

A weak, external scalar potential is taken to interact nonresonantly with a crystal with fixed ions. The electronic states are described by band theory. We do not make a self-energy correction to the band structure as we have done (in the form of a "scissors" operator) for semiconductors and α -quartz. The minimum LDA direct band gaps at the 6 integration points is 5.5 eV. Experimentally, the optical-absorption edges has been reported to be 5.7,¹⁸ 5.8,¹⁹ and 6.2 eV.²⁰ The required correction, apparently 0.3–0.8 eV for this system, is regarded as too

small and too poorly grounded theoretically to justify the large additional computational effort which would have been required.

The method is based on determining single-particle wave functions in a plane-wave basis using the pseudopotential method. First, a ground state is obtained using the method of Teter, Payne, and Allan;²¹ iterative methods for obtaining LDA ground states have been reviewed recently.²² Second, eigenstates are found by constructing a full matrix in the plane-wave basis, and using an iterative diagonalization subroutine to find the lowest 450 eigenstates. Third, the local field associated with linear response is found iteratively using the method of Ref. 23. Finally, nonlinear optical response is determined by various sums over states, as described in our earlier work.^{11,12} Successful production runs for this study took 100 h of computer time on an IBM 9000. The four steps described above took about 30%, 20%, 30%, and 20% of the CPU time, respectively.

The pseudopotentials were generated using a code written by Teter. The carbon, nitrogen, and oxygen pseudopotentials use two projection operators for each angular momentum, and match logarithmic derivatives over a larger range than is possible using the method of Hamann.²⁴ These pseudopotentials are also "optimally convergent" in the sense of Rappe and co-workers,²⁵ so first row elements can be handled with fewer plane waves. The hydrogen pseudopotential is also generated with Teter's code, but it is local.

To test the carbon pseudopotential, the static dielectric constant of diamond ϵ was calculated, using a plane-wave energy cutoff of 20 hartrees and 10 special²⁶ k points for the integration of the irreducible Brillouin zone. Our result for ϵ without a local-field correction is 6.02, compared to 6.06 for Hybertsen and Louie²⁷ who used the same integration points and a 25-hartree energy cutoff. The oxygen pseudopotential is the same one used successfully in the study of optical responses of α -quartz.^{28,29} The nitrogen pseudopotential was not explicitly tested.

To verify the utility of the hydrogen pseudopotential, an attempt was made to reproduce hydrogen atom splittings using the solid-state code. The use of the bare hydrogen potential $-1/r$ was also investigated. Based on a 24-hartree cutoff in a simple cubic cell 30 bohr on a side, the $1s$ - $2s$ eigenvalue splittings were below from the ideal value of 10.204 eV by 72 meV for the pseudopotential compared to 166 meV with the bare potential. The artificial splitting in the $2s$ - $2p$ manifold is 27 meV for the pseudopotential potential and 15 meV for the bare potential. The pseudopotential was chosen because its convergence properties were better than those of the bare potential for an E_{cut} near the operating point of this study.

The intent is to achieve a well-converged answer within the LDA. There are two parameters which determine the convergence: the energy cutoff E_{cut} and the number of k points in the Brillouin-zone integration $N_{k \text{ pt}}$. The energy cutoff was fixed at 25 hartrees for this study; this leads to an average of 6090 plane waves at each k point for this unit cell of volume 1020 cubic bohr. A 25-hartree energy cutoff was adequate to provide convergence in the case of α -quartz to about 31 meV in the ei-

genvalues and 0.02 units in ϵ_{∞} compared to a 30-hartree cutoff.²⁸⁻³⁰ As detailed in Table I, this apparently represents a convergence error of about 36 meV compared to a value extrapolated to full convergence. The carbon and nitrogen pseudopotentials will have better convergence properties than the oxygen pseudopotential, simply because the core charge is less in those cases. Larger energy cutoffs tend to lower the calculated value of ϵ_{∞} . To study the convergence with k points, we use one and six special integration points in the irreducible Brillouin zone, corresponding to $2 \times 2 \times 2$ and $4 \times 4 \times 4$ integration points, respectively, for the full Brillouin zone. For optical response in α -quartz, another wide-gap material, six such integration points were estimated to lead to integration errors of less than 0.5% in ϵ_{∞} .²⁹ The geometry is taken from Wyckoff.³¹ Geometric and other parameters of the calculation are given in Table II. Unfortunately, the scalar potential method does not produce all second-harmonic tensor components, but only the 10 linear combinations obtained by averaging over permutations of the indices.³² In certain cases, such as III-V semiconductors, this does not lead to a loss of information due to restrictions imposed by crystal symmetry. For Se and α -quartz, only one of two independent tensor components could be determined.^{13,28} In the case of urea, it is necessary to invoke Kleinman symmetry,³³⁻³⁵ which is appropriate far from resonance. Kleinman's symmetry condition ensures that far from resonances, each nonlinear optical susceptibility is equal to its index-permuted counterparts. However, this is exactly the restriction the scalar potential theory requires. For urea, this means $d_{123} = d_{312}$ or $d_{14} = d_{36}$ in the compressed notation. One would expect Kleinman symmetry to hold for urea for optical and lower frequencies, given the 6.0-eV band gap;¹ a calculation of the frequency dependence of the second-order susceptibility indicates this is true for the urea molecule.³⁶

III. RESULTS AND DISCUSSION

A. Absorption edge

The LDA direct band gaps at the six integration points are in the range of 5.5–6.2 eV. Experimentally, the

TABLE I. Eigenvalue convergence of α -quartz (SiO_2) as a function of the energy cutoff. These data are presented to illustrate the energy gap convergence of a system dominated by oxygen atoms. Silicon has a much softer pseudopotential, and will be completely converged for the values given in the table. The convergence is expected to be a property of the atom, hence the results obtained here are applicable to urea. The results for " ∞ " are those suggested by the Shanks (Ref. 43) extrapolation procedure. A convergence error of 36 meV due to oxygen at our operating point (25 hartree) is suggested from these data.

E_{cut} (hartree)	E_{gap} (eV)
20	5.934 55
25	6.149 24
30	6.180 18
∞	6.185

TABLE II. Parameters used in the calculation, except if a modification is specifically noted. The geometry is taken from Wyckoff (Ref. 31); the room-temperature lattice constant is used.

E_{cut}	25 hartrees		
N_{band}	426 conduction bands		
$N_{k \text{ pt}}$	6 in IBZ ($4 \times 4 \times 4$ in full BZ)		
a	5.622 Å		
c	4.716 Å		
		Wyckoff parameters	
H	0.2390	0.2610	0.2770
	-0.2390	0.7390	0.2770
	0.7390	0.2390	-0.2770
	0.2610	-0.2390	-0.2770
	0.1240	0.3760	0.0460
	-0.1240	0.6240	0.0460
	0.6240	0.1240	-0.0460
C	0.3760	-0.1240	-0.0460
	0	0.5	0.3308
	0.5	0	-0.3308
N	0.1419	0.3581	0.1857
	-0.1419	0.6419	0.1857
	0.6419	0.1419	-0.1857
	0.3581	-0.1419	-0.1857
O	0	0.5	0.5998
	0.5	0	-0.5998

optical-absorption edge has been reported to be 5.7,¹⁸ 5.8,¹⁹ and 6.2 eV.²⁰ In semiconductors, the LDA eigenvalues typically underestimate the band gaps by nearly 1 eV, with the figure rising for large-band-gap materials such as diamond.³⁷ Here, the band gap underestimate is only 300–800 meV, which is less than we expected for a material with such a large band gap.

One possibility is that the value used for E_{cut} , i.e., the number of plane waves used in the calculation, was too low to achieve the LDA limit. However, we have verified that the $1s$ - $2s$, $2p$ splitting of the hydrogen atom is reproduced to 72 meV by the pseudopotential, as indicated above. Moreover, using a fixed potential from our standard six k -point 25-hartree potential, we found the eigenvalues for one special point using a 25- and 30-hartree energy cutoff, using 6094 and 8021 plane waves, respectively. After setting the highest occupied eigenvalue to zero, the lowest 30 eigenvalues (of which 24 are occupied) differ by no more than 72 meV; the direct gap itself differs by 57 meV. This is consistent with the uncertainties expected for the oxygen and hydrogen pseudopotentials described in the previous section. Hence, more plane waves are not likely to open the band gap significantly, i.e., by more than about 100 meV.

Although we have used a self-energy corrected LDA band structure in past studies of optical response, we decided to forgo the correction in the present study. There is little guidance from realistic many-body calculations for organic crystals despite several studies for semiconductors. Perhaps urea is sufficiently different than the well-studied semiconductors that the energetics are different. A recent study of ice, like urea a hydrogen-bonded solid, indicates the need for gradient corrections to the LDA to obtain correct structural properties.³⁸ The importance of such corrections on optical properties is unclear; however, note that we use the experimental

geometry in this study. Another source of uncertainty is the fixed-ion approximation, which may be subject to correction due to hydrogen's zero-point motion or even the motion of entire urea molecules.

B. Linear optical responses

Our results for the linear response of urea for fixed ions at low frequencies are given in Table III, along with experimental values and another calculation. The experimental values seem reliable. For example, Kato³⁹ suggests that the extraordinary index of refraction is 0.016 units higher at 266 nm than given by the formula of Halbout *et al.*¹⁹

Our theory gives a good account of the data, but errors remain which are puzzling. Curiously, the local-field corrections, shown in Table IV, take our results away from experiment both in magnitude and in the ratio of ordinary and extraordinary polarization. A convergence study in the number of integration points appears in Table IV. The study is not conclusive, but we estimate our values for the dielectric constants are within 0.1 of the fully converged answers for the LDA. The results of a numerical evaluation of the f -sum rule for crystals is also given in Table IV. The difference of this value from unity is a measure of the overall quality of the calculation. Errors of a few percent are evident. Table V suggests that the retention of additional conduction-band states is unlikely to have a significant influence on the results for the dielectric constants. On the other hand, much of the missing oscillator strength for the f -sum rule is more likely contained in the higher bands rather than being associated with Brillouin-zone integration errors. Retaining as few as 10 bands is seen to be far from adequate for urea.

TABLE III. The static, fixed-ion, dielectric constants of urea, ϵ_∞ , calculated by various methods and given by experiments. The superscripts “o” and “e” mean “ordinary” and “extraordinary,” respectively. Curiously, the Adler-Wiser local-field corrections (Refs. 8 and 9) [including an exchange-correlation correction suitable for linearized LDA (Ref. 44)] do not improve the present calculation for this material. Similarly, a “self-energy correction” to increase the band gap, which is appropriate for semiconductors, would harm the agreement with experiment. The present results are presented for 6 integration points in the Brillouin zone.

	$\epsilon_\infty^{(o)}$	$\epsilon_\infty^{(e)}$	$\frac{\epsilon_\infty^{(o)} - 1}{\epsilon_\infty^{(e)} - 1}$
CNDO/S (Ref. 40)	1.28	1.66	0.42
Present LDA (no local field)	2.27	2.47	0.86
Present LDA	2.03	2.14	0.90
Experiment (Ref. 1)	2.17	2.49	0.78
Experiment (Ref. 34)	2.17		

An earlier complete neglect of differential overlap (CNDO) calculation⁴⁰ is seen to underestimate the dielectric constant severely, and differentially for the two components of the dielectric tensor. It is typical for semiempirical methods to underestimate dielectric constants in calculations for a variety of materials.

C. Second-harmonic response

Two independent reports of measurements of the nonlinear susceptibility for second-harmonic generation of the urea crystal have appeared.^{19,34} These measurements are in substantial agreement, as indicated in Table V. The report of Ref. 35 is substantially identical to that of Ref. 34, and hence does not appear to be a report of an independent measurement. The materials was measured earlier as a powder,⁴¹ but the resulting value is substantially higher than the consensus of the crystal measurements.

The dispersion from 1060 or 600 nm to the static limit is not significant given the substantial error bars, and the large band gap of urea. A molecular calculation suggests the value of d at 1064 nm is 5% higher than in the long-wavelength limit;³⁶ assuming a quadratic relationship in frequency, the 600-nm measurement would be 15% higher than the long-wavelength limit. Our values are in excellent agreement with both experiments, as indicated in Table VI, but not the early powder measurement.

There have been several calculations of the nonlinear susceptibility of crystalline urea based on calculations of the molecule. Calculations using the semiempirical method CNDO,³⁶ as well as Hartree-Fock⁶ are summa-

rized in Table VI. The CNDO calculation did not take into account intermolecular interactions in reporting their number. The authors state that the hydrogen bonds could cause significant changes in the computed result. The calculation of Zyss and Berthier⁶ addresses the effects of the chemical environment (in particular, including hydrogen bonding) of the urea molecule in a crystal, considering both isolated molecules and through the mutually consistent field (MCF) method. Zyss and Berthier perform a series of Hartree-Fock calculations with and without finite external fields, and use finite differences to determine the molecular polarizabilities and hyperpolarizabilities. The MCF calculations are Hartree-Fock with the molecules taken to be sitting in the electrostatic potential of all the other atoms in the crystal. Each atom is given a monopole charge, with the electrons being apportioned using a Mulliken localization procedure. Hence, the effects of electron delocalization due to band formation do not appear in the calculation, whereas the electrostatic interactions are treated.

The authors suggest that the MCF effects they considered are distinct from Lorentz local-field corrections. This is not clear to us. In any event, Zyss and Berthier⁶ do not present the results of the Lorentz local-field analysis suggested by Zyss and Oudar.⁴ The Lorentz correction would increase their (already too large) result by about a factor of 3.

As seen in Table VI, Zyss and Berthier report a 40% correction due to the interaction effects; the correction places their result farther from experiment, a factor of 2.4 too high, compared to being a factor of 1.5 too high without the correction. From their large interaction

TABLE IV. The static, fixed-ion, dielectric constants of urea, ϵ_∞ , as a function of the number of integration points in the irreducible Brillouin zone. Notation as in Table III. This table suggests that the error due to integration is about 2%. Additional k points would be more likely to increase the extraordinary dielectric constant slightly while leaving the ordinary dielectric constant relatively unchanged. Σ_f is the value of the integral f -sum rule, defined in Ref. 23. Ideally, this quantity is unity.

N_k pt	local field	$\epsilon_\infty^{(o)}$	$\epsilon_\infty^{(e)}$	$\Sigma_f^{(o)}$	$\Sigma_f^{(e)}$
1	no	2.270	2.439	0.956	0.945
6	no	2.270	2.473	0.956	0.961
1	yes	2.030	2.112		
6	yes	2.029	2.143		

TABLE V. A convergence study of ϵ_∞ as a function of the number of conduction bands (N_{band}) retained. This study was done for six integration points in the irreducible Brillouin zone. Σ_f as in Table IV. Deviations from unity are principally due to omitted conduction bands and errors in the Brillouin-zone integration. The figures suggest that the errors in ϵ_∞ due to the finite number of bands retained are less than 1%.

N_{band}	Local field	$\epsilon_\infty^{(o)}$	$\epsilon_\infty^{(e)}$	$\Sigma_f^{(o)}$	$\Sigma_f^{(e)}$
10	no	1.790	1.930	0.222	0.212
56	no	2.210	2.430	0.644	0.722
426	no	2.270	2.473	0.956	0.961
10	yes	1.678	1.721		
56	yes	2.007	2.111		
426	yes	2.029	2.143		

correction, they conclude that the assumption of oriented-gas approach must be questioned, at least for urea. Although we have a very different theoretical approach, we reach qualitatively similar conclusions in so far as our local-field effect (which is analogous to the intermolecular effects) is comparable to the long-wavelength result, which includes principally intermolecular effects.

The various terms contributing to the nonlinear response are given in Table VII, along with a sum rule for second-harmonic generation in insulating crystals^{12,32} which is seen to be satisfied numerically. The contributions are analyzed both in terms of direct excitations (cv), two-electron terms (ccv), and electron-hole terms (vvc), as well as whether the contribution is of zeroth (ϕ^0), first (ϕ^1), or second (ϕ^2) order in the local field. For semiconductors, the ccv - ϕ^0 term was always dominant. Here, it is still the largest, but it is of the same order of magnitude as the vvc - ϕ^1 term. Moreover, the ϕ^2 terms are small but significant, rather than negligible as they have been for other systems.^{12,28} The agreement between the integrals for one and six k points indicates that the Brillouin-zone integration is probably converged to within a few percent of its final value. The sum rule primarily tests the adequacy of $N_{k \text{ pt}}$, E_{cut} , and the number of bands retained for this system. The agreement between the one and six k -point integrals is further evidence that the Brillouin-

zone integration is adequate. Although problems remain at the level of a few percent, our earlier study on GaAs (Ref. 12) showed that convergence in the sum rule was more difficult to achieve than convergence in the value of $\chi^{(2)}$ itself. Hence, uncertainties associated with energy cutoffs are also a couple of percent. The local-field correction is seen to be very large for this material, some -89% of the final result. This is over three times larger in magnitude than the largest local-field corrections to second-harmonic generation which we have computed previously for other systems.^{11,12,13,28} The local-field correction is an important factor in obtaining agreement with the experimental results.

IV. CONCLUSION

Urea had previously been identified as a system in which both intramolecular and intermolecular effects are important for understanding its second-harmonic response, rendering the traditional "oriented-gas" assumption of additivity of the molecular hyperpolarizabilities β inapplicable to this system. We demonstrate that the LDA is capable of describing both the linear and second-harmonic response, but only if the local-field contributions are considered. As local fields are usually neglected in solid-state calculations, we suggest that neither traditional chemical nor physical methods suffice for

TABLE VI. The nonlinear susceptibility for second-harmonic generation of urea. $d = \frac{1}{2}\chi^{(2)}$. The value given for Ref. 19 is the suggested value of Ref. 42, based on a reconsideration of the reference standards for second-harmonic generation. The experiment of Ref. 34 was relative to potassium dihydrogen phosphate (KDP), but the value is given as per Ref. 45. The error bar for Ref. 34 is a minimum based on the significant digits given in the original report.

	λ (nm)	d (pm/V)
CNDO (Ref. 36)	1064	0.89
CNDO (Ref. 36)	∞	0.85
Isolated molecule (Ref. 6)	∞	1.8
Mutually consistent field (Ref. 6)	∞	2.9
Present LDA (no local field)	∞	2.1
Present LDA	∞	1.1
Expt. crystal (Ref. 19)	1060	1.2 ± 0.1
Expt. crystal (Ref. 34)	600	1.3 ± 0.3
Expt. powder (Ref. 41)	1060	7

TABLE VII. The terms contributing to the nonlinear susceptibility for second-harmonic generation (in pm/V). The classification scheme of Ref. 12 is used; the sum rule is also described in that reference. Terms in positive powers of ϕ are local-field corrections. The symbols “*cv*,” “*ccv*,” and “*vvc*” refer to single particle-hole pairs, two-electron terms, and electron-hole terms, respectively. Specifically, in the spectral sums, “*cv*” means one sum over conduction-band states and one sum over valence states are performed, “*ccv*” means two sums over conduction-band states and one over valence states are performed, and “*vvc*” means one sum over conduction-band states and two sums over valence states are performed. Ideally the total sum rule should be 0; its possible range is -2 to 2 .

N_k pt		ϕ^0 terms	ϕ^1 terms	ϕ^2 terms	$d = \frac{1}{2}\chi^{(2)}$	Σ_p
1	<i>cv</i>	-0.04	-0.00		-0.04	-0.017
	<i>ccv</i>	2.17	0.42	-0.04	2.56	-0.966
	<i>vvc</i>	-0.04	-1.59	0.22	-1.41	1.017
	total	2.10	-1.17	0.18	1.11	0.034
6	<i>cv</i>	-0.04	0.00		-0.04	-0.017
	<i>ccv</i>	2.23	0.42	-0.04	2.62	-0.965
	<i>vvc</i>	-0.05	-1.62	0.22	-1.45	1.018
	total	2.14	-1.19	0.18	1.13	0.036

the calculation of second-harmonic susceptibility in crystalline urea. Even if convergence issues or physical effects not considered herein modify our quantitative results in the future, we suggest that it is unlikely that any mechanisms will diminish the importance of the local-field corrections estimated in this study: this, rather than the quantitative agreement we have obtained, is the principal result of this paper. We conjecture that local-field will provide order 1 corrections for all organic crystals

which contain an intramolecular π system and hydrogen bonds.

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