Semi-empirical correction algorithm for AC-9 measurements in a coccolithophore bloom

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Values for the coefficients of absorption (a) and attenuation (c) obtained from AC-9 measurements in coccolithophore blooms do not provide satisfactory inputs for radiance transfer models. We have therefore modified the standard AC-9 scattering correction algorithm by including an extra term, $F(\lambda, \lambda_r)$, which allows for possible wavelength dependence in the scattering phase function. We estimated the magnitude of $F(\lambda, \lambda_r)$, which is unity in the standard algorithm, by adjusting the absorption and scattering values in Hydrolight radiance transfer calculations until the depth profiles of downward irradiance (E_d) and upward radiance (L_u) matched those measured *in situ*. The modified algorithm was tested with data from a phytoplankton bloom dominated by the coccolithophore *Emiliania huxleyi*, which occurred in the western English Channel in May 2001. In this paper, we only have sufficient data to adequately constrain the radiance transfer model in one wave band centered on 488 nm. A single value of $F(\lambda, \lambda_r) = 1.4$ was found to produce satisfactory agreement between modeled and observed profiles at four widely spaced stations within the bloom. Measurements of the ratio of backscattering (b_b) to total scattering (b) showed significant wavelength dependence at these stations. © 2003 Optical Society of America

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1. Introduction

Coccolithophore blooms are of considerable biogeochemical significance[1] and are readily observed in remote sensing images.[2] The optical properties of coccolithophore cells and detached liths have been widely investigated *in situ*[3–5] and in laboratory cultures,[6] but attempts to model their scattering phase functions have met with limited success.[7] Moreover, a recent paper[8] has drawn attention to the difficulty of interpreting AC-9 (WetLabs) measurements of inherent optical properties (IOPs) made inside a coccolithophore bloom. In this instance a better match between modeled and measured radiometric parameters was obtained with a semi-analytic model for IOPs rather than AC-9 *in situ* measurements. This observation raises questions concerning the appropriate correction of AC-9 measurements made in coccolithophore blooms and in other turbid environments.

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2. Theory

The standard scattering correction algorithm for AC-9 absorption measurements, derived by Zaneveld *et al.*,[9] is based upon three hypotheses:

1. The fraction of scattered light not collected by the absorption meter, k_a, is independent of wavelength.
2. The fraction of scattered light collected by the attenuation meter, k_c, is independent of wavelength.
3. There exists a reference wavelength, λ_r, at which absorption by materials other than water is negligible.

For this paper we shall accept the third hypothesis, with the reservation that it appears to hold for a variety of marine particles[10] but may not be tenable for very high chromophoric dissolved organic matter concentrations. However, if we assume that the AC-9 absorption sensor collects light scattered only at angles between zero and some critical angle θ_{ca}, and write k_a and k_c as explicit functions of wavelength, then

$$k_a(\lambda) = 2\pi \int_{\theta_{ca}}^{\pi} \tilde{\beta}(\psi, \lambda)\sin(\psi)d\psi\,, \tag{1}$$

where $\tilde{\beta}(\psi, \lambda)$ is the scattering phase function. Similarly, if the attenuation sensor collects light scattered up to a critical angle θ_{cc}, then

$$k_c(\lambda) = 2\pi \int_0^{\theta_{cc}} \tilde{\beta}(\psi, \lambda)\sin(\psi)d\psi\,. \quad (2)$$

It follows that an assumption of wavelength-independent behavior of k_a and k_c (hypotheses 1 and 2) implies that the scattering phase function ($\tilde{\beta}$) is constant over all visible wavelengths. If we allow the possibility of wavelength dependence, the derivation of Zaneveld *et al.* produces

$$a_n(\lambda) = a_i(\lambda) - a_i(\lambda_r)\,\frac{c_i(\lambda) - a_i(\lambda)}{c_i(\lambda_r) - a_i(\lambda_r)} \times \left[\frac{k_a(\lambda)}{1 - k_a(\lambda) - k_c(\lambda)} \Big/ \frac{k_a(\lambda_r)}{1 - k_a(\lambda_r) - k_c(\lambda_r)}\right], \quad (3)$$

where the subscripts n and i refer to nonwater and uncorrected instrument output respectively. Equation (3) can be rewritten as

$$a_n(\lambda) = a_i(\lambda) - a_i(\lambda_r)\,\frac{c_i(\lambda) - a_i(\lambda)}{c_i(\lambda_r) - a_i(\lambda_r)}\,F(\lambda, \lambda_r)\,, \quad (4a)$$

where

$$F(\lambda, \lambda_r) = \left[\frac{k_a(\lambda)}{1 - k_a(\lambda) - k_c(\lambda)} \Big/ \frac{k_a(\lambda_r)}{1 - k_a(\lambda_r) - k_c(\lambda_r)}\right]. \quad (4b)$$

In the wavelength-independent case $k_a(\lambda) = k_a(\lambda_r)$ and $k_c(\lambda) = k_c(\lambda_r)$, and $F(\lambda, \lambda_r) = 1$. However, measurements on a population of particles for which hypotheses 1 and 2 were not true would require a value of $F(\lambda, \lambda_r)$ other than unity. The fact that $F(\lambda, \lambda_r)$ does not depend upon the magnitude of the scattering signal means that once an appropriate value has been determined for a given population of particles it can be used regardless of changes in concentration. The retention of the explicitly wavelength-dependent correction factor $F(\lambda, \lambda_r)$ in Eq. (4) serves two purposes. As a free parameter whose magnitude can be empirically determined, it allows AC-9 measurements to be adjusted until they provide satisfactory inputs for radiance transfer models. As a diagnostic feature, its systematic behavior can be used to indicate a requirement to consider additional spectral effects in AC-9 correction procedures. In either case, the obvious way to determine the magnitude of $F(\lambda, \lambda_r)$ is to determine the value that it must assume in order to achieve closure between radiance transfer models and *in situ* radiometric measurements. This procedure is followed in the present paper.

3. Materials and Methods

Data for this work were obtained during a cruise off the Scilly Isles (English Channel) between the 20 May and 25 May 2001. A coccolithophore bloom was encountered approximately 20 km southeast of the islands, and a total of four stations were occupied within the bloom.

A. IOP Measurements

A 25-cm-pathlength WetLabs AC-9 was used to measure the absorption coefficient (a_n) and beam attenuation coefficient (c_n) of materials other than water at 9 wave bands (10 nm FWHM) across the visible spectrum. Optical blanks for the AC-9 were measured regularly with use of ultrapure Millipore water treated with ultraviolet light, and calibration of the two optical channels remained within the manufacturer's specifications of $\pm 0.005\ \text{m}^{-1}$. Absorption and attenuation signals at 715 nm were corrected for temperature-dependent water absorption,[11] and the data were averaged over 1-m depth intervals. Equation 4(a) was used to explore the sensitivity of the scattering correction error $F(\lambda, \lambda_r)$ values that were varied systematically between 1 and 1.8 in 0.1 steps. Total backscattering (b_b) was measured at 470 and 676 nm using a Hydroscat-2 (HobiLabs). Since calibration of this instrument is currently not possible in our laboratory, it was assumed that the manufacturer's calibration remained valid.

B. Radiometric Measurements

Downward irradiance (E_d) and upward radiance (L_u) were measured in seven wave bands (10 nm FWHM) across the visible spectrum with use of a Satlantic Sea-viewing Wide Field of View Sensor Profiling Multi-Channel Radiometer (SPMR). The SPMR was deployed at a distance at least 20 m from the ship in order to avoid shadowing. A deck reference measuring surface irradiance (E_s) at the same seven wave bands was mounted on the superstructure of the ship. The stability of the SPMR and deck reference irradiance sensors was monitored at the start and the end of the cruise with a 100-W standard lamp, and the SPMR radiance sensors were checked with the same lamp to illuminate a Spectralon reflectance target. All sensors remained within factory specifications. Signals from the SPMR were processed using ProSoft, a Matlab module supplied by the manufacturers. Data processing steps included the application of calibration constants and averaging over 1-m-depth intervals.

C. Radiance Transfer Modeling

Radiance transfer within the coccolithophore bloom was simulated with the Hydrolight (Sequoia) software package. Absorption and scattering coefficients were derived from AC-9 measurements, with separate runs being carried out for AC-9 files generated using different values of $F(\lambda, \lambda_r)$ for the modified scattering correction algorithm [Eq. 4(a)]. Fournier-Forand[12] scattering phase functions for each station and depth were chosen with use of Hydroscat-2 values for the backscattering coefficient. Surface irradiance data from the SPMR deck reference was supplied for each station. The test for a successful model was that both downwards irradiance and up-

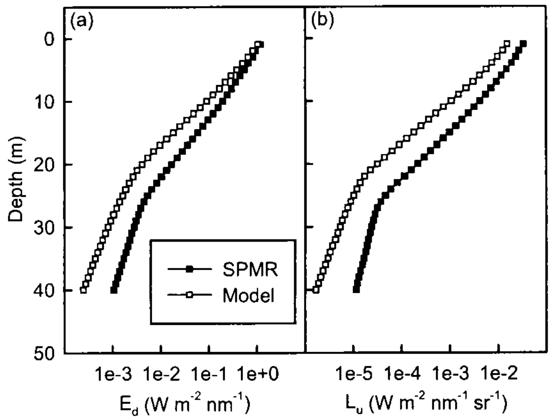

Fig. 1. Profiles of modeled and measured (a) E_d and (b) L_u for station 12. The model uses standard AC-9 IOPs and shows systematic underestimates of both radiometric parameters with depth.

wards radiance values from the Hydrolight output should accurately match *in situ* measurements from the SPMR. This procedure requires b_b to be specified and is subject to error in the presence of significant inelastic scattering or fluorescence. The Hydroscat-2 measures b_b at 470 and 676 nm, but the 676-nm wave band overlaps the chlorophyll *a* fluorescence peak. The analysis in this paper is therefore restricted to AC-9 measurements at 488 nm and Hydroscat-2 measurements at 470 nm. We assume that the standard correction algorithm suffices for AC-9 measurements at 676 nm, since this is close to the 715-nm reference wavelength.

4. Results

Figure 1 shows profiles of measured and modeled downwards irradiance (E_d) and upwards radiance (L_u) at 490 nm, for station 12, which was located 15 km inside the coccolithophore bloom. The model profile was obtained with use of AC-9 inputs with the standard correction procedure [i.e., $F(\lambda, \lambda_r) = 1.0$]. Modeled values are lower than measured values except for E_d close to the surface, where surface irradiance measurements were used as an input to the model. Assuming that the simulations are properly constrained (i.e., all of the boundary conditions are adequately parameterized), Fig. 1 suggests that there is an error in one or more of the measurements of IOPs used in the simulation. Exploratory simulations of the effect of varying b_b values (not shown) indicated that it is unlikely that errors in backscattering can account for the observed discrepancy. An overestimate of the absorption coefficient, on the other hand, would have the observed effect of reducing E_d too rapidly as a function of depth and would also result in the underestimation of L_u values. This overestimate can be corrected by an appropriate choice of value for $F(\lambda, \lambda_r)$. Figure 2 shows plots of modeled-versus-measured values of E_d and L_u at 490 nm for the top 20 m of station 12 and for a range of values of $F(\lambda, \lambda_r)$. The upper bound of $F(\lambda, \lambda_r) = 1.8$

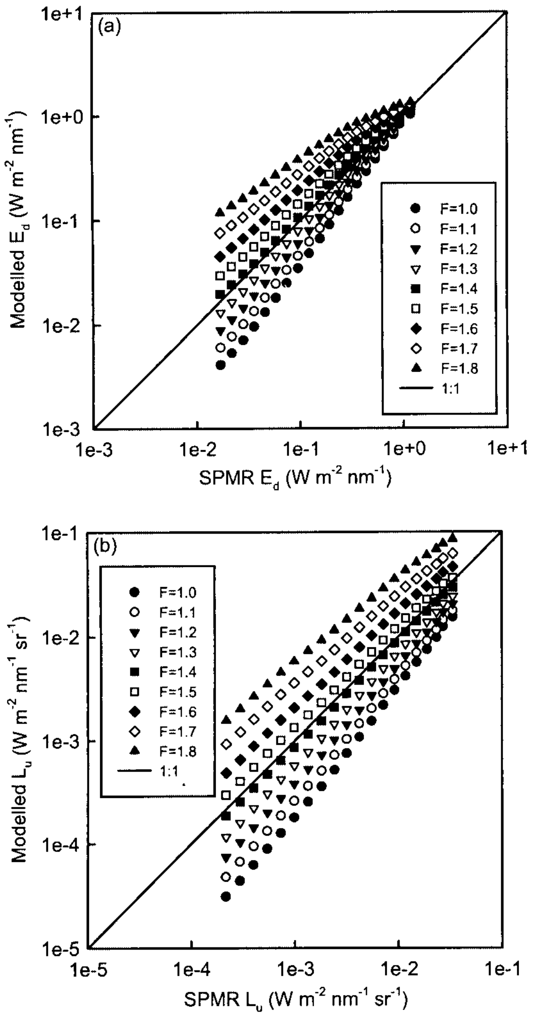

Fig. 2. Plots of modeled versus measured (a) E_d and (b) L_u for a range of values of $F(\lambda, \lambda_r)$ for station 12. For this station a value of $F(\lambda, \lambda_r) = 1.4$ provides the best match between modeled and measured radiometry.

is set by the criteria that $a_n(\lambda) \geq 0$. For both E_d and L_u, the data series closest to the 1:1 lines in Fig. 2 corresponds to the same value of $F(\lambda, \lambda_r) = 1.4$. The quality of the match between modeled and measured radiometry for $F(\lambda, \lambda_r) = 1.4$ appears to be good over the range of depths (0–20 m) corresponding to coccolithophore-rich water at this station.

Figure 3 shows the average standard percentage errors for E_d and L_u at 490 nm for the top 20 m of station 12 plotted as a function of $F(\lambda, \lambda_r)$. The average standard percentage error, ϵ, can be defined as

$$\epsilon = \frac{\sum_n |(x_{\text{in}} - x_{\text{mod}})/x_{\text{in}}| \times 100}{n}, \tag{5}$$

where n is the number of observations, x_{in} refers to *in situ* measurements, x_{mod} refers to modeled values, and x is the parameter being investigated (either E_d or L_u). The minimum error for both E_d and L_u estimation occurs for $F(\lambda, \lambda_r) = 1.4$ and is of the order of

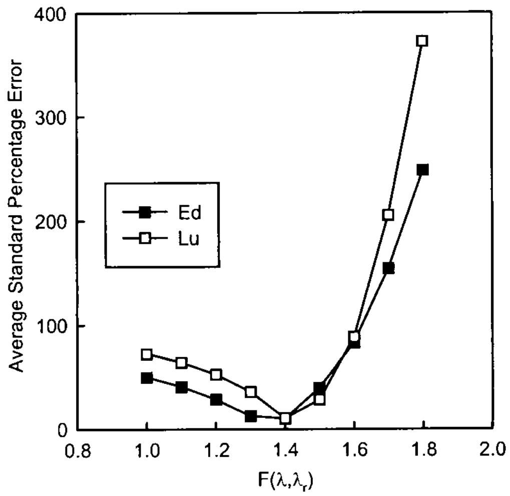

Fig. 3. Standard percentage error between modeled and measured values of E_d and L_u, averaged over all depths in the surface layer of station 12, is minimal at $F(\lambda, \lambda_r) = 1.4$ for both L_u and E_d.

10%. This compares to errors of the order of 50% and 70% for E_d and L_u, respectively, for simulations based upon standard AC-9 inputs [$F(\lambda, \lambda_r) = 1.0$]. The fact that a single value of $F(\lambda, \lambda_r)$ minimizes the error in both E_d and L_u simultaneously is a good indication that the form of the scattering correction algorithm suggested in Eq. 4(a) is correct.

The effect of setting $F(\lambda, \lambda_r) = 1.4$ on the values of the AC-9 IOPs at 488 nm is shown in Fig. 4. Modified values of $a_n(488)$ are significantly lower than standard AC-9 values throughout the water column, with the greatest differences occurring in the highly scattering coccolithophore layer, which extends down to 20 m. For this station the discrepancy between standard and modified $a_n(488)$ reaches values as great as 0.07m^{-1}, which corresponds to percentage differences of up to almost 50%. This result confirms that of Smyth *et al.*,[8] who found that a similar level of error in AC-9 absorption was necessary to obtain satisfactory closure between measurements and simulations for data obtained in a coccolithophore bloom. The magnitude of the error in the absorption measurement is determined by the residual absorption at 715 nm [$a_i(\lambda_r)$ in Eq. 3], which is a function of the scattering coefficient. Hence the largest discrepancies between modified and standard AC-9 absorption values occur at depths with the highest scattering coefficients. Figures 4(b) and 4(c) serve to illustrate the knock-on effects of errors in the absorption measurement. As the scattering coefficient is derived from $b_n(\lambda) = c_n(\lambda) - a_n(\lambda)$, a decrease in the value of $a_n(\lambda)$ results in an increase in $b_n(\lambda)$ by the same amount. Since the scattering signal is roughly 1 order of magnitude greater than the absorption signal for this station, the percentage error induced in the scattering signal is much lower (approximately 5%). Finally, a decrease in the magnitude of $a_n(488)$ increases the $b_n(488)$ signal by 5% and also reduces the backscattering ratio by approximately 5%.

Three stations other than station 12 were occupied within the same bloom. Figure 5 shows plots of modeled and measured E_d and L_u for these other stations as well as for station 12. The simulations shown were based upon AC-9 data at 488 nm corrected with $F(\lambda, \lambda_r) = 1.4$. In all cases this produced matches between measured and modeled values of E_d and L_u that were a significant improvement over simulations that used the standard AC-9 correction with $F(\lambda, \lambda_r) = 1.0$. The effect of setting $F(\lambda, \lambda_r) = 1.4$ was to reduce the magnitude of $a_n(488)$ values by up to 50%.

If the scattering phase function is indeed wavelength independent, then one would expect that the backscattering ratio would be equal at two different wavelengths. Figure 6 shows that the backscattering ratio in the blue is systematically higher than in the red for coccolithophore-rich waters at all four stations. Since these *in situ* results are not consistent with the observation of Voss *et al.*[6] that the normal-

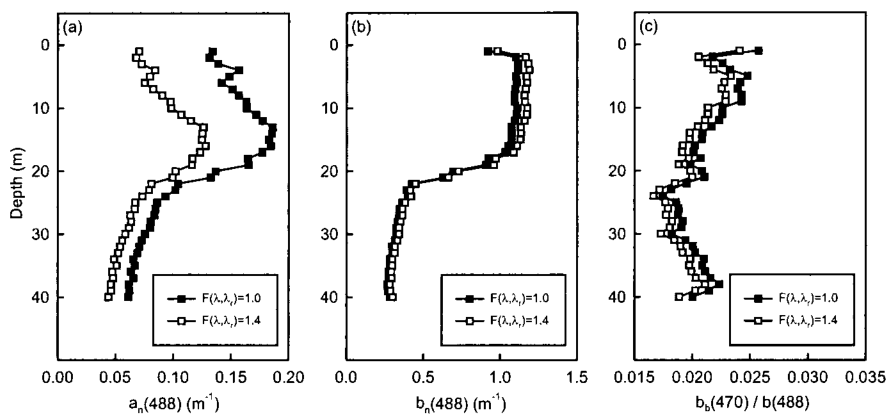

Fig. 4. Depth profiles of standard [$F(\lambda, \lambda_r) = 1.0$] and modified [$F(\lambda, \lambda_r) = 1.4$] (a) AC-9 absorption at 488 nm, (b) AC-9 scattering at 488 nm, and (c) backscattering ratio in the blue (Hydroscat-2 b_b at 470 nm and AC-9 b at 488 nm). Changing the value of $F(\lambda, \lambda_r)$ in the scattering correction for AC-9 absorption also has an impact on the AC-9 scattering coefficient and thus also affects the value of backscattering ratio.

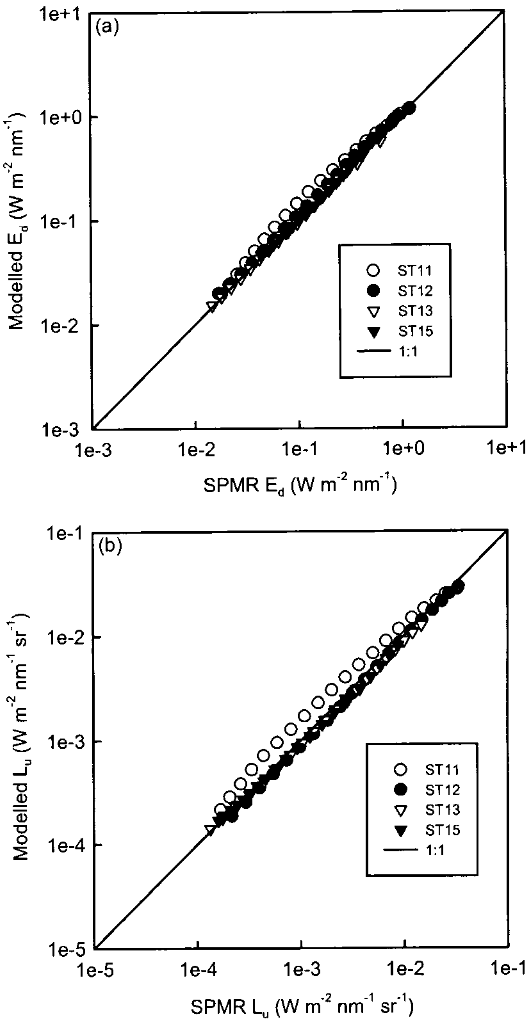

Fig. 5. Plots of modeled versus measured (a) E_d and (b) L_u for four stations inside a coccolithophore bloom. Modeled radiometry comes from Hydrolight simulations performed with use of AC-9 data that had been corrected with a value of $F(\lambda, \lambda_r) = 1.4$ in all cases.

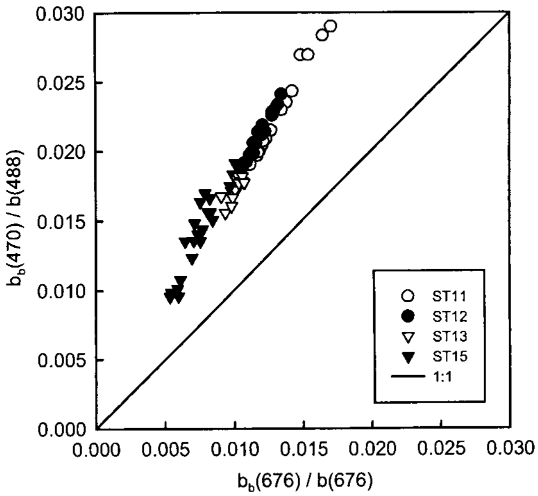

Fig. 6. Backscattering ratio in the blue is systematically higher than backscattering ratio in the red for four stations in coccolithophore-rich waters. Blue backscattering ratios are based upon Hydroscat-2 readings at 470 nm and AC-9 scattering values at 488 nm corrected with $F(\lambda, \lambda_r) = 1.4$.

ized volume scattering function for cultures of *Emiliania huxleyi* showed "no significant spectral dependency," it is likely that more extensive studies of phase functions in highly scattering waters are required.

5. Discussion

Kirk[13] used Monte Carlo modeling to assess the performance of reflecting tube absorption meters, and found that the measured absorption (a_m) would always be greater than the true absorption (a). He also showed that the ratio a_m/a increased linearly with the ratio of scattering to absorption (b/a), with the slope determined by the scattering phase function of the sample. The results presented in this paper are consistent with Kirk's analysis. The object is not to downplay the usefulness of the AC-9. As Zaneveld *et al.*[9] state: "The reader should not conclude that the *in situ* devices are less accurate than spectrophotometers, simply because we analyse the errors. . . .Even the best (spectrophotometer) models do not collect all the scattered light and the method of analysis used below would apply to them also." The implication, however, is that the standard scattering correction algorithm for AC-9 absorption measurements is not applicable to data collected in coccolithophore-rich waters. A modified algorithm, of the form of Eq. 4(a), with $F(\lambda, \lambda_r) = 1.4$ for $\lambda = 488$ nm provides sets of AC-9 data that generate significantly superior matches between measured and modeled radiometry. It is suggested that use of $F(\lambda, \lambda_r) = 1.4$ rather than $F(\lambda, \lambda_r) = 1.0$ (the standard algorithm) will provide AC-9 operators with improved quality absorption and scattering data at 488 nm when working within a coccolithophore bloom. Values of $F(\lambda, \lambda_r)$ still need to be derived for other wavelengths, but this requires a knowledge of the spectral dependency of b_b, which is not currently available.

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