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Reply

Reply to Comment on "Computing molecular electrostatic potentials with the PRISM algorithm"

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Abstract

This Reply clarifies the similarities and differences between our work and that of Gadre et al. in computing ab initio molecular electrostatic potentials. The principal advance described by us was to cast the PRISM algorithm for two-electron repulsion integrals in a form suitable for the calculation of molecular electrostatic potentials.

In the foregoing Comment [1], Gadre and Shirsat (henceforth GS) maintain that a Letter [2] recently published by us in this Journal presents results which are essentially similar to work of Gadre et al. [3–8] published between 1989 and 1992. We have carefully examined all of the arguments which GS present and we certainly do not wish to understate the value of the contributions which Gadre and his co-workers have made in this area. However, we disagree with the opinions expressed in their Comment. Primarily, it appears that these opinions stem from a failure to grasp the most important feature of the methodology described in ref. [2], viz. the use of the PRISM algorithm [9,10] to compute the necessary three-center Coulomb integrals: GS ignore this completely and yet it is the high efficiency of our PRISM implementation which is principally responsible for the performance of our program. GS raise additional objections to our Letter and we respond to these below.

In the second and fourth paragraphs of their Comment, GS note that (like theirs) our program begins by looping over pairs of shells in order to eliminate any which are numerically insignificant. This cutoff strategy results in only $\mathcal{O}(N)$ significant shell pairs and is a standard feature of all modern integral programs. The use of such cutoffs has a long history [11–17] and can be traced back at least as far as Clementi's seminal work in the 1960s.

The fifth and sixth paragraphs of the Comment by GS compare the upper bound formula used by us with those of Gadre et al. Our approach begins with the rigorous least upper bound embodied in Eq. (2) of ref. [2]. For total angular momentum $L>0$, this bound cannot be expressed in closed form and must be evaluated by numerical methods [18]. This may be contrasted with the upper bounds employed by Gadre et al. which, while rigorous and amenable to closed-form expression, are not least bounds except for $L=0$. Our bound therefore constitutes a significant improvement over those of Gadre et al.

The remaining paragraphs of the Comment by GS (parallel and PC implementations, timings) are not relevant to the content of our Letter [2] and therefore we have no comment on them.

We hope that this Reply clarifies the similarities and differences between our work and that of Gadre et al.

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The principal advance described by us in ref. [2] was to cast the PRISM algorithm for two-electron repulsion integrals in a form suitable for the calculation of molecular electrostatic potentials.

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