

Perdew, Burke, and Ernzerhof Reply: Our goal in Ref. [1] was to present a simple, nonempirical derivation of a simplified generalized gradient approximation (GGA) for the exchange-correlation energy of density functional theory. Among the many conditions that might have been imposed to construct the functional, we selected as most appropriate to the GGA form those already satisfied by the local spin density (LSD) approximation, or by the numerical GGA derived from sum rules on the exchange-correlation hole [2].

One of the conditions already satisfied by LSD is the Lieb-Oxford bound [3]. By satisfying this bound locally (and *only* by so doing), we ensure that our GGA will satisfy the integrated bound for *any* possible electron density, as LSD does. The resulting GGA Perdew-Burke-Ernzerhof (PBE) is remarkably like the more complicated Perdew-Wang 1991 GGA derived from the sum rules. Simple physical arguments [4] explain its characteristic dependencies upon the local density, spin polarization, and reduced density gradient, and its characteristic chemical effects [5].

Zhang and Yang [6] modify the large-gradient limit of the PBE exchange energy, the least-determined aspect of GGA. The PBE parameter κ , which controls this limit, is intrinsically fuzzy or nonuniversal, as discussed in Refs. [1,2,4,7]. By relaxing the strict Lieb-Oxford bound and fitting κ instead to exact exchange energies of atoms, they obtain a “revPBE” GGA which yields more accurate energies for atoms and covalent molecules. This semiempirical modification may be useful for those interested primarily in such systems, but our original version is nearly optimal as a *widely applicable* GGA for *both* quantum chemistry and condensed-matter physics. The GGA form is severely limited. Revision of the derived GGA cannot simultaneously satisfy quantum chemists who want it to be more nonlocal [6] and solid state physicists who want it to be more local [7,8]. Fitting one kind of situation too closely, e.g., atoms and covalent bonds, may worsen the results for very different situations, e.g., for crystalline lattice constants [7–9], hydrogen bonds [10], or binding-energy curves of rare-gas dimers [11], complexes [12], and molecular crystals [13].

Even among covalent bonds, the fit of Ref. [6] has a procrustean aspect: It improves the energetics of most multiple bonds by worsening many single bonds (cf., CH₄ and H₂O). Improved atomization energies can also be achieved via nonempirical exact-exchange mixing [14,15].

In Table I, we show that the modified PBE, which significantly improves upon the PBE for the atomization energies of N₂, NO, and O₂, worsens the bond lengths of these systems compared to PBE.

TABLE I. Bond lengths in bohr from LSD, PBE [1], revPBE [6] functionals, and experimental values [1].

Molecule	LSD	PBE	revPBE	Expt.
H ₂	1.447	1.418	1.413	1.401
CH ₄	2.074	2.071	2.073	2.052
N ₂	2.071	2.084	2.089	2.072
NO	2.169	2.189	2.196	2.175
O ₂	2.279	2.306	2.313	2.281
F ₂	2.618	2.672	2.685	2.678

To users who want simple but well-founded density functionals of wide applicability, we recommend LSD and (at a higher level) the “GGA made simple” of Ref. [1]. To developers of density functionals, we recommend a search for energy densities at \mathbf{r} that depend upon higher derivatives of the density, or upon the density at all \mathbf{r}' .

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