# Supplementary Information

to accompany

"Restoring the density-gradient expansion for exchange in solids and surfaces"

by

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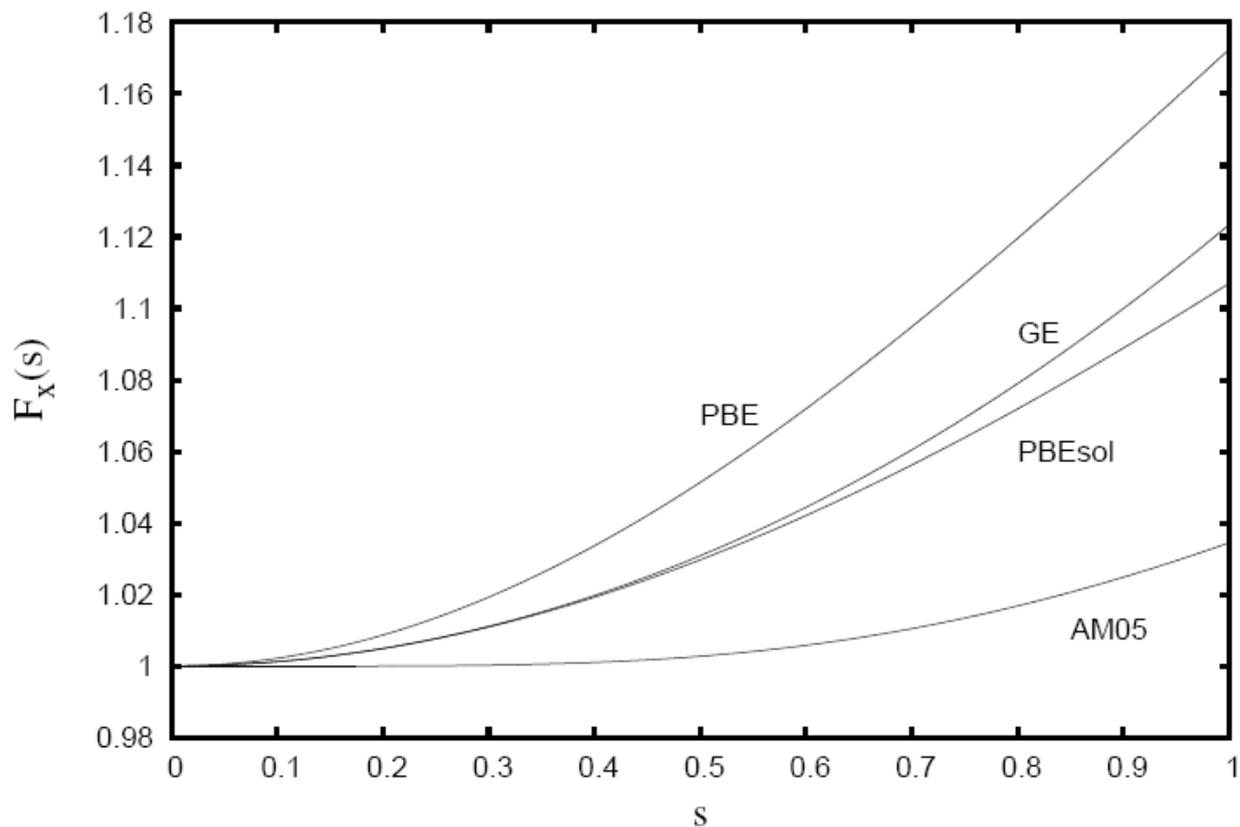Physical Review Letters

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Fig. S1. Exchange-only enhancement factors $F_x(s)$ in the range $0 \leq s \leq 1$ for the gradient expansion (GE) and for the generalized gradient approximations PBE, AM05 (Ref. [12]), and PBEsol. AM05 and LAG (Ref. [11]) exchange are based on the Airy gas model, proposed as a paradigm by W. Kohn and A.E. Mattsson, Phys. Rev. Lett. **81**, 3487 (1998). A similar figure for $F_x(s)$ comparing Wu-Cohen (Ref. [6]) and PBE is given in Fig. 1 of Ref. [6].
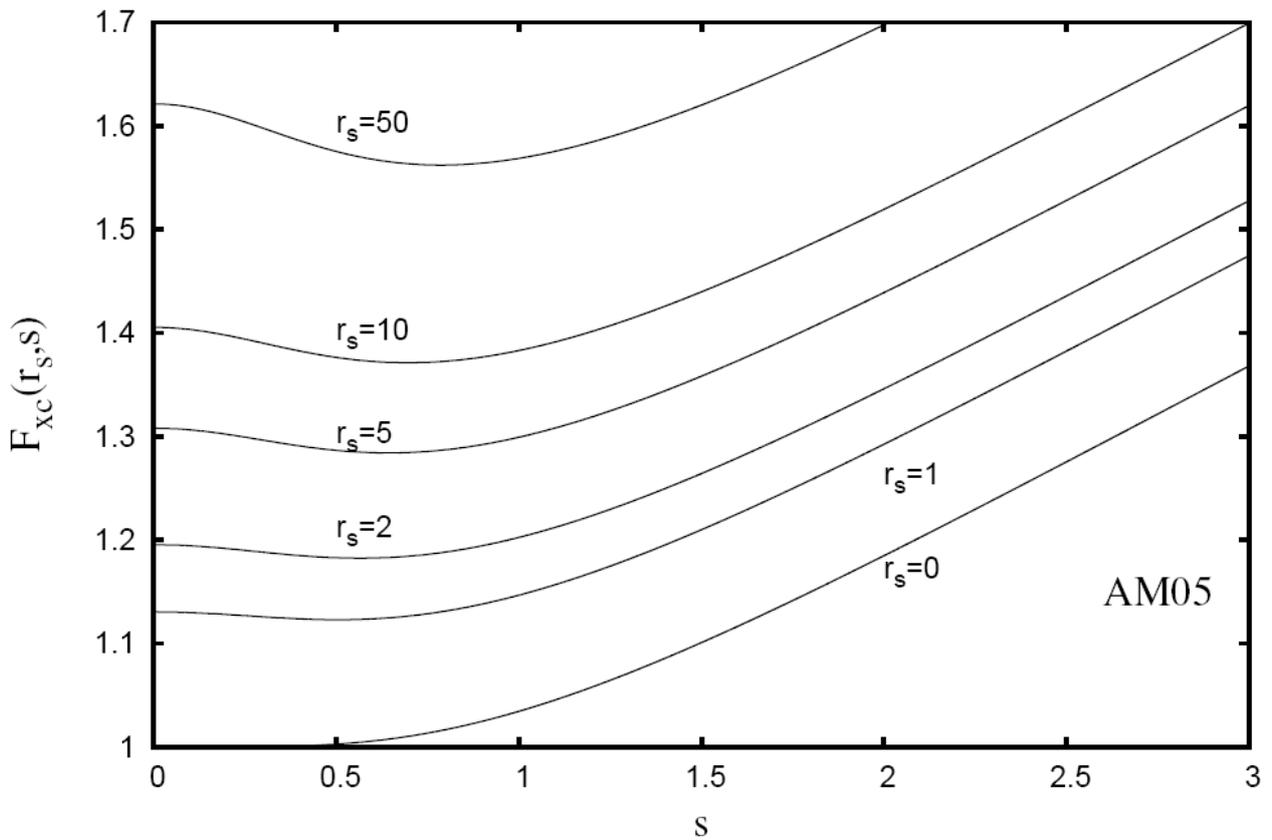
Fig. S2. Enhancement factor of the generalized gradient approximation AM05 (Ref. [12]), for comparison with those of PBE and PBEsol in Fig. 2 of our article. For s<3, AM05 is more "local" in the $r_s \rightarrow 0$ or exchange-only limit, but it shows more similarity to PBEsol in the range $1 \leq r_s \leq 10$ and $s \leq 1$ relevant to valence electrons in many solids. For an even more diminished gradient dependence, see Fig. 1 of G.I. Csonka, O.A. Vydrov, G.E. Scuseria, A. Ruzsinszky, and J.P. Perdew, J. Chem. Phys. **126**, 244107 (2007).
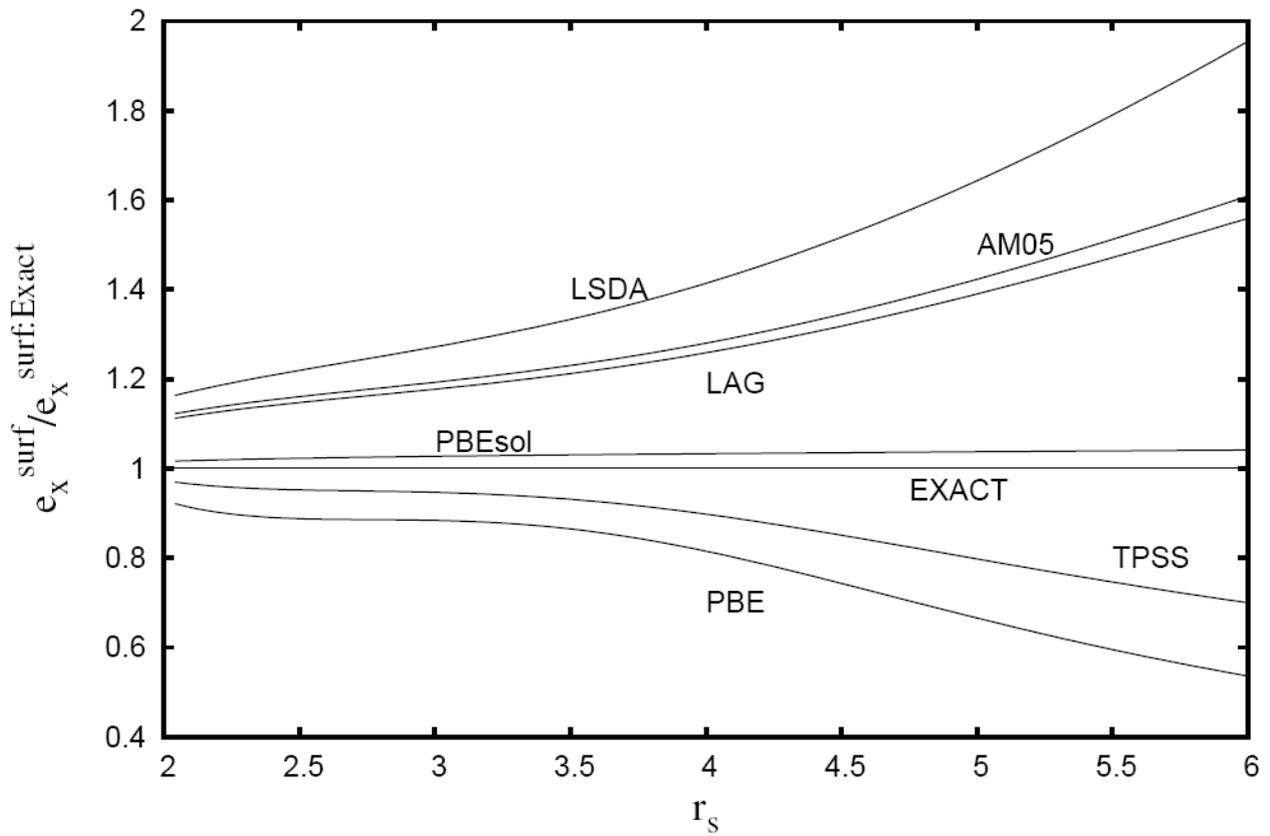
Fig. S3. Ratios of approximate to exact surface exchange energies of jellium, calculated on LSDA densities with the functionals of our article plus LAG (Ref. [11]) and AM05 (Ref. [12]). Note the remarkable accuracy of PBEsol over the whole range of bulk densities $2<r_s<6$. Wu-Cohen values, from Table VI of Ref. [6], are slightly less accurate than TPSS values. Exact exchange values from J.M. Pitarke and A.G. Eguiluz, Phys. Rev. B **63**, 045116 (2001). Interpolation on $r_s$ by the formula of L.M. Almeida, J.P. Perdew, and C. Fiolhais, Phys. Rev. B **66**, 075115 (2002).

| Solid | LSDA | PBE | TPSS | PBEsol | Expt-ZPAE |
|-------|------|-----|------|--------|-----------|
| Li | 3.383 | 3.453 | 3.475 | 3.453 | 3.451 |
| Na | 4.049 | 4.199 | 4.233 | 4.159 | 4.210 |
| K | 5.093 | 5.296 | 5.362 | 5.232 | 5.212 |
| Al | 4.008 | 4.060 | 4.035 | 4.038 | 4.020 |
| C | 3.537 | 3.579 | 3.579 | 3.562 | 3.556 |
| Si | 5.410 | 5.479 | 5.466 | 5.442 | 5.423 |
| SiC | 4.355 | 4.404 | 4.394 | 4.381 | 4.349 |
| Ge | 5.634 | 5.776 | 5.744 | 5.693 | 5.646 |
| GaAs | 5.626 | 5.772 | 5.745 | 5.687 | 5.643 |
| NaCl | 5.471 | 5.696 | 5.696 | 5.611 | 5.580 |
| NaF | 4.505 | 4.700 | 4.706 | 4.633 | 4.594 |
| LiCl | 4.968 | 5.146 | 5.113 | 5.072 | 5.090 |
| LiF | 3.904 | 4.063 | 4.026 | 4.002 | 3.987 |
| MgO | 4.178 | 4.270 | 4.247 | 4.229 | 4.197 |
| Cu | 3.530 | 3.635 | 3.593 | 3.578 | 3.596 |
| Rh | 3.791 | 3.871 | 3.846 | 3.819 | 3.793 |
| Pd | 3.851 | 3.950 | 3.917 | 3.888 | 3.877 |
| Ag | 3.997 | 4.129 | 4.076 | 4.045 | 4.064 |

Table SI.    Equilibrium lattice constants (Å) of our 18 test solids. For error summaries, see Table I of our article. The zero-point anharmonic expansion (ZPAE) was subtracted from the experimental zero-temperature values (Ref. [28]). For C, Si, SiC, Ge, GaAs, and MgO, the basis sets were taken from J. Heyd, J.E.Peralta, G.E.Scuseria, and R. L. Martin, J. Chem. Phys. **123**,174101 (2005). For the rest of the solids, the basis sets and effective core potentials from Ref. [28] were used. For AM05 (Ref. [12]) lattice constants, see http://dft.sandia.gov/functionals/AM05.html. Very recent tests of AM05 have been made by A.E. Mattsson, R. Armiento, J. Paier, G. Kresse, J.M. Wills, and T.R. Mattsson, J. Chem. Phys. **128**, 084714 (2008). For Wu-Cohen (Ref. [6]) lattice constants, see Refs. [6] and [13]. (These other studies do not correct the experimental value for ZPAE.)

|        | LSDA  | PBE   | TPSS  | PBEsol | EXP   |
|--------|-------|-------|-------|--------|-------|
| SiH4   | 15.04 | 13.58 | 14.47 | 14.04  | 13.98 |
| SiO    | 9.70  | 8.49  | 8.1   | 8.89   | 8.33  |
| S2     | 8.82  | 4.98  | 4.71  | 5.36   | 4.41  |
| C3H4   | 34.78 | 31.27 | 30.68 | 32.52  | 30.56 |
| C2H2O2 | 32.74 | 28.84 | 27.58 | 30.27  | 27.46 |
| C4H8   | 56.54 | 50.63 | 50.11 | 52.84  | 49.82 |

Table SII.  Atomization energies (eV) of the six AE6 molecules of Ref. [29]. For error summaries, see Table II of our article. AM05 (Ref. [12]) values could not be computed, since a spin-polarized version of AM05 has not been published. Wu-Cohen (Ref. [6]) atomization energies are given in Ref. [13].

|        | LSDA | -       | PBEsol  | PBE     |
|--------|------|---------|---------|---------|
| M      | 0    | 0.12346 | 0.12346 | 0.21951 |
| B      | 0    | 0.06673 | 0.046   | 0.06673 |
| $r_s$=2 | 3354 | 3493    | 3374    | 3265    |
| $r_s$=3 | 764  | 813     | 774     | 741     |
| $r_s$=4 | 261  | 286     | 267     | 252     |
| $r_s$=6 | 53   | 63      | 56      | 52      |

Table SIII. Surface exchange-correlation energy $\sigma_{xc}$ (in erg/cm$^2$) for jellium with bulk density parameter $r_s$, as a function of the exchange gradient coefficient $\mu$ and the correlation gradient coefficient $\beta$ in the PBE form. The proper coefficients for the gradient expansion are $\mu$= 0.12346 and (in the high-density limit) $\beta$=0.06673. In the random phase approximation (RPA), $\beta$ is nearly independent of $r_s$. Beyond RPA, $\beta$ is 0.06673 at $r_s$=0, but around 0.059 at $r_s$=3 and 0.051 at $r_s$=6 (C.D. Hu and D.C. Langreth, Phys. Rev. B **33**, 943 (1986)).

|        | LSDA   | -       | PBEsol  | PBE     |
|--------|--------|---------|---------|---------|
| $\mu$  | 0      | 0.12346 | 0.12346 | 0.21951 |
| $\beta$ | 0     | 0.06673 | 0.046   | 0.06673 |
| Na     | 4.049  | 4.196   | 4.159   | 4.199   |
| Si     | 5.410  | 5.431   | 5.442   | 5.479   |
| MgO    | 4.178  | 4.229   | 4.229   | 4.270   |
| Pd     | 3.851  | 3.879   | 3.888   | 3.950   |
| ME     | -0.055 | 0.007   | 0.003   | 0.048   |
| MAE    | 0.055  | 0.014   | 0.028   | 0.053   |

Table SIV. Bulk lattice constant *a* (in Angstrom) for four solids, as a function of the exchange gradient coefficient $\mu$ and the correlation gradient coefficient $\beta$ in the PBE form. The difference between PBE and LSDA lattice constants is believed to arise largely in a higher-density region of core-valence overlap (M. Fuchs, M. Bockstedte, E. Pehlke, and M. Scheffler, Phys. Rev. B **57**, 2134 (1998)). Note that restoring the gradient expansion for exchange in the PBE form is *by itself* sufficient to correct the too-long PBE lattice constants, without fitting the surface energy.