Supplementary material for "Kohn-Sham potentials in exact density-functional theory at non-integer electron numbers"

This text contains supplementary material for "Kohn-Sham potentials in exact density-functional theory at non-integer electron numbers"[1].

I. FITTING OF THE QMC DENSITY

Atom	Cation	Neutral	Anion
Li	7.2800 ± 0.00002	7.4781 ± 0.00006	7.5007 ± 0.00008
C	37.4259 ± 0.0004	37.8354 ± 0.0005	37.8795 ± 0.0005
F	99.0772 ± 0.0007	99.7189 ± 0.0007	99.8443 ± 0.0007

TABLE I. Absolute ground-state DMC energies.

We fit the electron density of the atoms and ions to a function

$$n^M(r) = (1+r)^{g-1} \sum_{\kappa=1}^{n} \frac{a_0^\kappa + a_1^\kappa r^2}{b_0^\kappa + r^2} e^{-K^\kappa r}, \qquad (1)$$

where $K^1 = 2k$, $K^{\kappa>1} > K^1$ and

$$k = \sqrt{-2\epsilon_h^M}, \qquad g = \frac{Z+1-M}{k}. \qquad (2)$$

This fitting function ensures that the density obeys the correct asymptotic behaviour [2]

$$\lim_{r\to\infty} \frac{\frac{1}{2}\nabla^2\sqrt{n^M(r)}}{\sqrt{n^M(r)}} = -\frac{Z+1-M}{r} - \epsilon_h^M, \qquad (3)$$

where $-\epsilon_h = \frac{1}{2}k^2$ is the second and first ionisation potential, or electron affinity of atom A for ions A^+, A and A^- respectively.

Normalisation of n was carried out after fitting to the QMC data, to ensure that the electron number was preserved according to the appropriate abcissae and weights. QMC ground-state energies [reported in Table I] were used to calculate I and A. Values for the second ionisation potential came from the NIST database [3].

Parameters used for the fiting function (1) are shown in Appendix A and were found by minimising

$$\int_0^\infty [n^M(r) - n^M_{\rm QMC}(r)]^2 (Zr + r^2) {\rm d}r, \qquad (4)$$

where $n^M_{\rm QMC}$ is calculated in diffusion Monte Carlo (DMC) with Jastrow full-valence complete-active-space wave functions fully optimized at the variational Monte Carlo level [4]. The local errors from the fitted functions are less than the statistical error of the QMC calculations in the inner region, while the outer region matches exactly the QMC affinity or ionisation potential (IP) or experimental second IP.

II. ADDITIONAL MESH PLOTS

In the main text we illustrate the derivative discontinuity and other unusual features of the KS potential directly by plotting $v_{\rm s}^{Z+c}(r)$ as a function of radius r and excess electron number $c = N - Z$. By noting that the Hartree potential $v_{\rm H}^{Z+c}(r) = \int \frac{{\rm d}\boldsymbol{r}'}{|\boldsymbol{r}-\boldsymbol{r}'|} n^{Z+c}(r')$ must be piecewise continuous as a function of c (since n is piecewise continuous) and the external potential $v_{\rm Ext}(r)$ is independent of c we see that these features must manifest in $v_{\rm xc}^{Z+c}(r) = v_{\rm s}^{Z+c}(r) - v_{\rm Ext}(r) - v_{\rm H}^{Z+c}(r)$. We thus show, in Figure 1 plots of $v_{\rm xc}^{Z+c}(r)$ for the three species to highlight in greater detail some of its important features. We include also $v_{\rm Hxc}^{Z+c}(r)$ to show the total internal effective potential.

III. APPROXIMATION TO $V_{\rm S}^N$

In equation (16) of the text we propose an approximation

$$n^N(\boldsymbol{r}) v_{\rm s}^N(\boldsymbol{r}) \approx (1-f) n^M(\boldsymbol{r}) [v_{\rm s}^{M^-}(\boldsymbol{r}) + \Delta^M] + f n^{M+1}(\boldsymbol{r}) v_{\rm s}^{M+1^-}(\boldsymbol{r}) \qquad (5)$$

which relates the KS potential at fractional electron number N to its values at adjacent integers. In Figure 2 we show the potential at r =1, 2, 4 and 8 for $-1 < c \leq 1$. It is clear, at least for these selected values of r, that the approximation is very good. To reduce numerical errors we use Δ^M calculated numerically via $\Delta^M = \int {\rm d}\boldsymbol{r} n^M(\boldsymbol{r}) [v_{\rm s}^{M+0.01}(\boldsymbol{r}) - v_{\rm s}^M(\boldsymbol{r})]/M$ in all cases. For $M = Z$ this gives results within 3 mhartree of the theoretical prediction $I - A$.

In Figure 3 we show mesh plots of the difference between the approximate and actual Kohn-Sham potentials. We note that there are numerical issues in the QMC density and in the Kohn-Sham inversion algorithm for $r \to 0$ and $r \to \infty$. We suspect that some of the error in these regions is due to this numerical noise. This is exemplified by $c \to -1$, where the fit should become almost exact, but clearly shows significant numerical deviation in all cases, but especially Li.

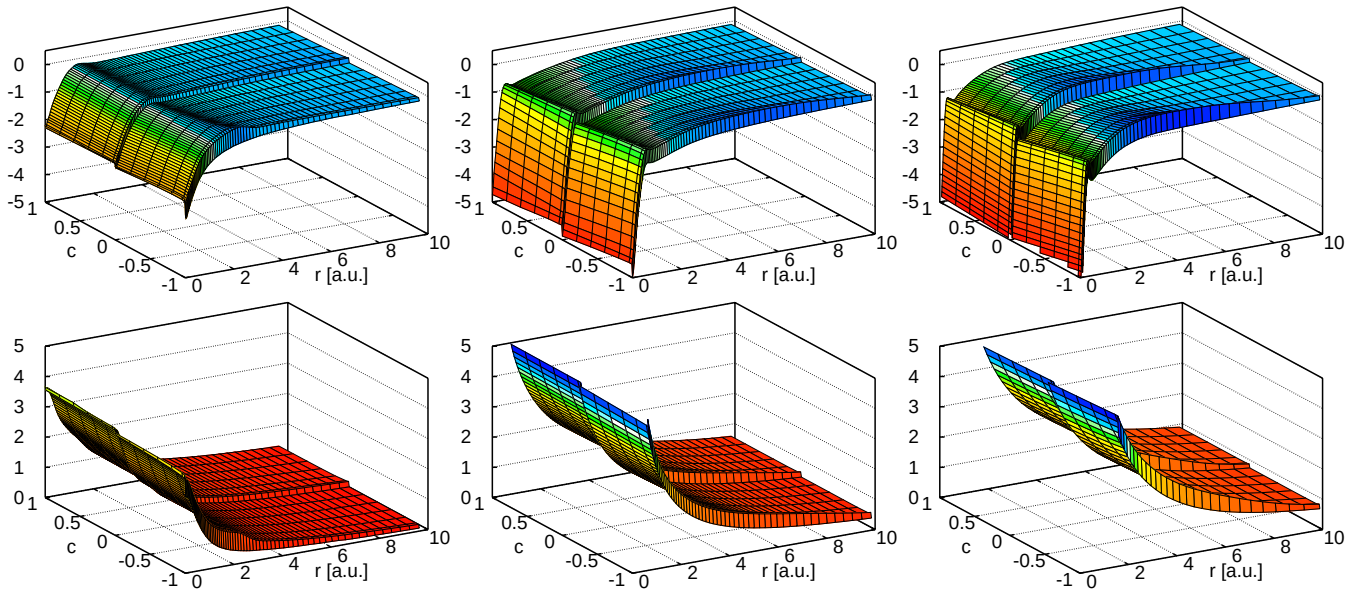

FIG. 1. xc potentials $v_{\rm xc}^{Z+c}(r)$ (top) and Hxc potentials $v_{\rm Hxc}^{Z+c}(r)$ (bottom) as a function of the radial distance r and the fractional excess electron number $c = N - Z$ for Li (left), C (middle) and F (right).

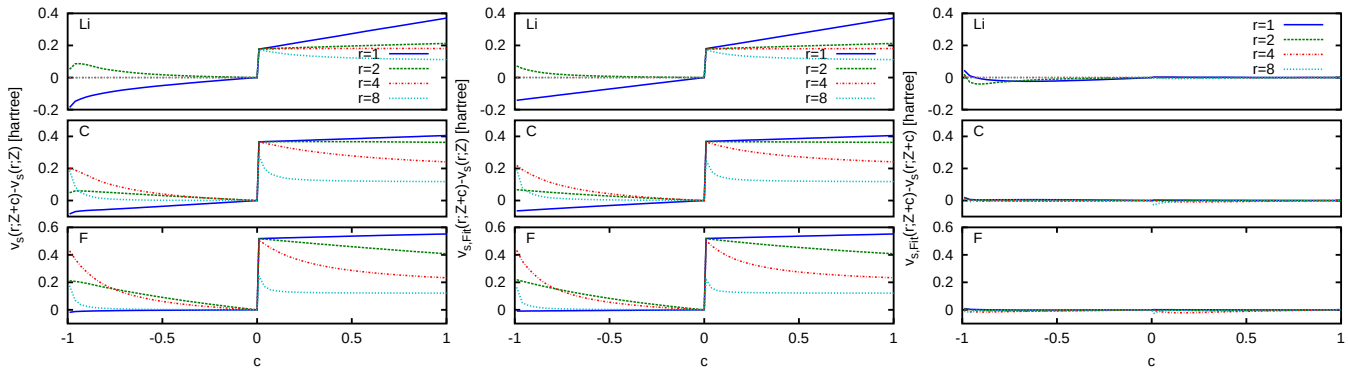

FIG. 2. Comparison of $v_{\rm s,approx}^{Z+c}(r)$ [from equation 16 of main text or (5) here] with $v_{\rm s}^{Z+c}(r)$ obtained from inversion. Left plot shows $v_{\rm s}^{Z+c}(r)$ (the same as Figure 2 in the paper), middle plot shows $v_{\rm s,approx}^{Z+c}(r)$, and right columnn shows their difference.

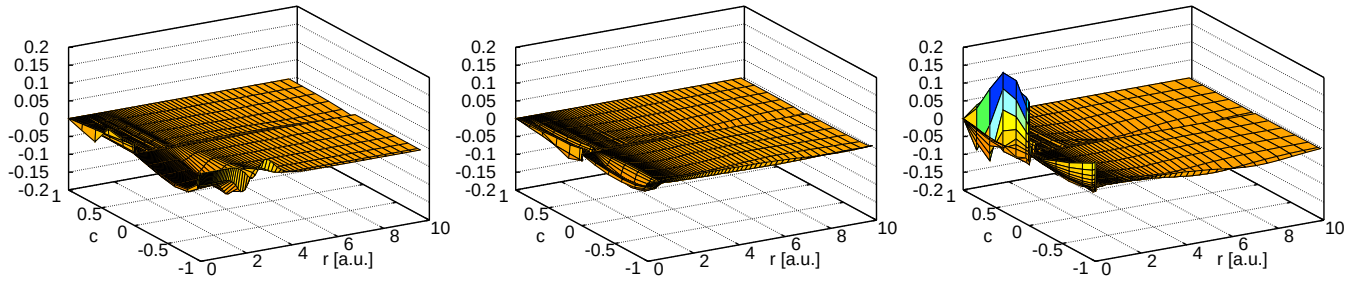

FIG. 3. $v_{\rm s,approx}^{Z+c}(r) - v_{\rm s}^{Z+c}(r)$ for Li (left), C (middle) and F(right).

Appendix A: Tables of fitting parameters

We provide here the parameters found by fitting the QMC density by the function given in Eq. 1.

1. Fitting parameters for Li ions.

Li^+: g, ϵ_h	0.8488	-2.7757		
a_0^1, a_1^1, b_0^1, K^1	0.3087	3.1382	0.1358	4.7123
a_0^2, a_1^2, b_0^2, K^2	0.6979	5.4662	0.1078	4.8464
a_0^3, a_1^3, b_0^3, K^3	0.6332	5.4767	0.1267	7.4059
Li: g, ϵ_h	1.5887	-0.1981		
a_0^1, a_1^1, b_0^1, K^1	0.0000	0.0368	0.0000	1.2589
a_0^2, a_1^2, b_0^2, K^2	0.0193	-0.0663	0.0444	1.7221
a_0^3, a_1^3, b_0^3, K^3	0.1859	6.1006	0.0649	5.6060
a_0^4, a_1^4, b_0^4, K^4	1.0550	6.5475	0.1004	7.8585
Li^-: g, ϵ_h	0.0000	-0.0227		
a_0^1, a_1^1, b_0^1, K^1	-0.0000	0.3789	0.0000	0.4261
a_0^2, a_1^2, b_0^2, K^2	0.6442	-0.9637	0.1445	0.9173
a_0^3, a_1^3, b_0^3, K^3	1.1321	13.2649	0.4060	4.6360
a_0^4, a_1^4, b_0^4, K^4	0.6203	4.3880	0.0989	6.3464

2. Fitting parameters for C ions.

C^+: g, ϵ_h	1.4938	-0.8963		
a_0^1, a_1^1, b_0^1, K^1	0.0038	0.5181	0.2303	2.6778
a_0^2, a_1^2, b_0^2, K^2	0.2244	2.4283	0.1614	3.1094
a_0^3, a_1^3, b_0^3, K^3	0.5551	-5.9399	0.1294	4.6394
a_0^4, a_1^4, b_0^4, K^4	2.0413	-8.6682	0.1346	7.2725
a_0^5, a_1^5, b_0^5, K^5	2.6932	26.9625	0.1116	11.5265
a_0^6, a_1^6, b_0^6, K^6	6.8900	64.3988	0.0827	15.0396
C: g, ϵ_h	1.1050	-0.4095		
a_0^1, a_1^1, b_0^1, K^1	-0.0230	0.2497	0.0724	1.8100
a_0^2, a_1^2, b_0^2, K^2	0.1274	1.9700	0.1031	2.3832
a_0^3, a_1^3, b_0^3, K^3	0.5945	-6.6976	0.1653	4.6147
a_0^4, a_1^4, b_0^4, K^4	1.6819	-8.1982	0.1044	7.0917
a_0^5, a_1^5, b_0^5, K^5	3.0723	44.8323	0.1063	10.6443
a_0^6, a_1^6, b_0^6, K^6	6.7880	56.5449	0.0873	14.3063
C^-: g, ϵ_h	0.0000	-0.0441		
a_0^1, a_1^1, b_0^1, K^1	0.0162	0.1622	0.0099	0.5940
a_0^2, a_1^2, b_0^2, K^2	0.4331	3.7392	0.0711	1.3221
a_0^3, a_1^3, b_0^3, K^3	1.0876	-17.8857	0.0919	3.6025
a_0^4, a_1^4, b_0^4, K^4	2.2450	16.7874	0.1066	8.0515
a_0^5, a_1^5, b_0^5, K^5	3.4417	38.3274	0.1032	10.0188
a_0^6, a_1^6, b_0^6, K^6	5.5813	30.2854	0.1050	13.6394

3. Fitting parameters for F ions.

F^+: g, ϵ_h	1.2472	-1.2857		
a_0^1, a_1^1, b_0^1, K^1	-0.0483	1.8761	0.0117	3.2071
a_0^2, a_1^2, b_0^2, K^2	0.4731	13.0823	0.0995	4.0844
a_0^3, a_1^3, b_0^3, K^3	1.3455	-12.2877	0.1049	7.2343
a_0^4, a_1^4, b_0^4, K^4	6.5853	-73.0653	0.0841	9.6721
a_0^5, a_1^5, b_0^5, K^5	3.0913	-69.6398	0.1197	15.0256
a_0^6, a_1^6, b_0^6, K^6	29.5182	129.0790	0.0886	21.3125
F: g, ϵ_h	0.8827	-0.6417		
a_0^1, a_1^1, b_0^1, K^1	-0.0349	1.1718	0.0081	2.2657
a_0^2, a_1^2, b_0^2, K^2	0.3246	13.2959	0.0862	3.4734
a_0^3, a_1^3, b_0^3, K^3	1.8434	-16.5528	0.0804	7.9333
a_0^4, a_1^4, b_0^4, K^4	3.5155	-37.2971	0.0817	8.4666
a_0^5, a_1^5, b_0^5, K^5	6.9788	-63.2687	0.0968	11.8701
a_0^6, a_1^6, b_0^6, K^6	28.1609	24.6661	0.0905	21.1531
F^-: g, ϵ_h	0.0000	-0.1254		
a_0^1, a_1^1, b_0^1, K^1	0.0122	0.7452	0.0021	1.0016
a_0^2, a_1^2, b_0^2, K^2	0.6640	16.3921	0.0382	2.3493
a_0^3, a_1^3, b_0^3, K^3	2.8523	-51.0754	0.0994	6.9453
a_0^4, a_1^4, b_0^4, K^4	2.3037	-54.2370	0.1006	7.0417
a_0^5, a_1^5, b_0^5, K^5	4.1322	-31.2873	0.1015	10.8156
a_0^6, a_1^6, b_0^6, K^6	7.6164	-86.0300	0.0891	13.3094
a_0^7, a_1^7, b_0^7, K^7	22.6386	30.0281	0.0924	20.6210

[1] T. Gould and J. Toulouse, ArXiv e-prints , 1407.2707 (2014).
[2] M. Levy, J. P. Perdew, and V. Sahni, Phys. Rev. A **30**, 2745 (1984).
[3] A. Kramida, Yu. Ralchenko, J. Reader, and NIST ASD Team, NIST Atomic Spectra Database (ver. 5.1), [Online]. Available: `http://physics.nist.gov/asd` [2014, March 8]. National Institute of Standards and Technology, Gaithersburg, MD. (2013).
[4] J. Toulouse, R. Assaraf, and C. J. Umrigar, J. Chem. Phys. **126**, 244112 (2007).