

Reply to ‘‘Comment on ‘Significance of the highest occupied Kohn-Sham eigenvalue’’’

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I give an additional argument that the proof of Perdew *et al.*, stating that the highest occupied Kohn-Sham eigenvalue equals the ionization energy, is flawed. I also argue that the new proof given by Perdew and Levy in the preceding paper is wrong. The significance of the result for the two-electron ‘‘Hooke’s atom’’ is then discussed. [S0163-1829(98)04103-4]

Using a mixed state density functional,

$$\tilde{E}^{(N)}[\tilde{\rho}_N] = (1 - \omega)E^{(M)}[\rho_M] + \omega E^{(M+1)}[\rho_{M+1}], \quad (1)$$

where

$$\tilde{\rho}_N(\mathbf{r}) = (1 - \omega)\rho_M(\mathbf{r}) + \omega\rho_{M+1}(\mathbf{r}), \quad (2)$$

the tilde indicates a mixed state quantity, $\int \tilde{\rho}_N d\mathbf{r} = N = M + \omega$, M is an integer, and $0 < \omega < 1$, Perdew *et al.*¹⁻³ gave a proof that ϵ_{M+1} , the highest occupied Kohn-Sham⁴ (KS) eigenvalue (for the exact KS potential only), equals $-I$, where the ionization energy $I = E^{(M)}[\rho_M] - E^{(M+1)}[\rho_{M+1}]$. They took

$$\tilde{\rho}_N(\mathbf{r}) = \sum_i \tilde{f}_i^{(N)} |\psi_i(\mathbf{r})|^2 \quad (3)$$

with $\tilde{f}_i^{(N)} = 1$ for $i \leq M$, $\tilde{f}_{M+1}^{(N)} = \omega$ and $\tilde{f}_i^{(N)} = 0$ for $i > M + 1$ and equated $d\tilde{E}^{(N)}/d\omega = -I$ with $d\tilde{E}^{(N)}/d\tilde{f}_{M+1}^{(N)} = \epsilon_{M+1}$, where the last equality is just Janak’s⁵ theorem.

In the preceding paper Perdew and Levy⁶ (PL) say that I (in Ref. 7) seem to question the validity of Janak’s theorem for ensembles with noninteger particle number. Janak’s theorem must hold, providing the KS potential v_{KS} which yields $\tilde{\rho}_N(\mathbf{r})$ is obtainable as the functional derivative of $\tilde{E}_{\text{Hxc}}^{(N)}[\tilde{\rho}_N] + \int v(\mathbf{r})\rho_N(\mathbf{r})d^3r$, where $v(\mathbf{r})$ is the external potential and $\tilde{E}_{\text{Hxc}}^{(N)}[\tilde{\rho}_N]$ is the Hartree, exchange, and correlation part of $\tilde{E}^{(N)}[\tilde{\rho}_N]$. Because of the dependence of $\tilde{\rho}_N$ on ω in Eq. (2), I argued that $\delta\tilde{E}_{\text{Hxc}}^{(N)}/\delta\tilde{\rho}_N + v(\mathbf{r})$ might not be $v_{KS}(\mathbf{r})$. If, as PL state, the variation of $\tilde{\rho}_N$ is constrained to keep N (and thus ω) fixed, my argument no longer holds. I showed⁷ that $d\tilde{E}_H^{(N)}/d\tilde{f}_{M+1}^{(N)} \neq d\tilde{E}_H^{(N)}/d\omega$, indicating that $d/d\tilde{f}_{M+1}^{(N)}$ and $d/d\omega$ do not represent the same thing but PL argue that $d\tilde{E}^{(N)}/d\tilde{f}_{M+1}^{(N)} = d\tilde{E}^{(N)}/d\omega$ in no way implies that the equality holds for the component parts of $\tilde{E}^{(N)}$. However, given the fixed N condition, I can now argue that the two derivatives are never equivalent. We have that

$$d\tilde{E}^{(N)}/d\omega = \lim_{\delta N \rightarrow 0} \{\tilde{E}^{(N+\delta N)}[\tilde{\rho}_{N+\delta N}] - \tilde{E}^{(N)}[\tilde{\rho}_N]\} / \delta N, \quad (4)$$

whereas

$$d\tilde{E}^{(N)}/d\tilde{f}_{M+1}^{(N)} = \lim_{\delta N \rightarrow 0} \{\tilde{E}^{(N)}[\tilde{\rho}_{N+\delta N}] - \tilde{E}^{(N)}[\tilde{\rho}_N]\} / \delta N. \quad (5)$$

Equation (4) contains the difference between $N + \delta N$ and N electron functionals whereas in Eq. (5) $\tilde{E}^{(N)}[\tilde{\rho}_N]$ is evaluated twice, first at $\tilde{\rho}_N$ and then at $\tilde{\rho}_{N+\delta N}$ where $\delta N = \delta\tilde{f}_{M+1}^{(N)}$. This is much like taking a pure state functional $E^{(M)}[\rho_M]$ which has no physical meaning for noninteger M , and differentiating it with respect to one of the f_i . This yields⁵ ϵ_i which everyone agrees is physically meaningless (except for the highest occupied ϵ_i , whose meaning or lack thereof is the center of our dispute).

PL give a new proof that $\epsilon_{M+1} = -I$ based on their Eqs. (19A) and (19B),

$$\mu = \partial\tilde{E}_{\text{sg}}^{(N)}/\partial N = \partial\tilde{E}_{\text{sg}}^{(N)}/\partial\omega = \partial\tilde{E}_g^{(N)}/\partial N = \partial\tilde{E}_g^{(N)}/\partial\omega. \quad (6)$$

Here $\tilde{E}_g^{(N)}$ is given by Eq. (1) as is $\tilde{E}_{\text{sg}}^{(N)}$ except that $v_{KS}(\mathbf{r})$ is treated as an external potential for the pure states so that $E_{\text{sg}}^{(M)}$ and $E_{\text{sg}}^{(M+1)}$ just equal the sum of their occupied eigenvalues. Because it must be calculated self-consistently, v_{KS} is not equivalent to an external potential. It is obvious that $E_{\text{sg}}^{(M)} \neq E_g^{(M)}$ and that the chemical potential $\mu = E_g^{(M+1)} - E_{\text{sg}}^{(M)} \neq E_{\text{sg}}^{(M+1)} - E_{\text{sg}}^{(M)}$. Thus the claim of PL that $\mu = \partial\tilde{E}_g^{(N)}/\partial N$ is identical to $\partial\tilde{E}_{\text{sg}}^{(N)}/\partial N$, where the latter derivative is evaluated with $\tilde{v}_{KS}^{(N)}$ taken to be independent of N , cannot be correct. I note that $v_{KS}^{(M+1)} \neq v_{KS}^{(M)}$ and that even when these are taken to be fixed external potentials, $\tilde{v}_{KS}^{(N)}$ cannot be independent of N because it approaches $v_{KS}^{(M+1)}$ as $\omega \rightarrow 1$ and $v_{KS}^{(M)}$ as $\omega \rightarrow 0$.

In a note added in proof to Ref. 7 I pointed out that $d\tilde{E}_H^{(N)}/d\tilde{f}_{M+1}^{(N)}$ fails to equal $d\tilde{E}_H^{(N)}/d\omega$ only because the relaxation energy is not quite linear in $(1 - \tilde{f}_{M+1}^{(N)})$. The many-body wave functions from which the charge density and then the ‘‘exact’’ $v_{KS}(\mathbf{r})$ are obtained to numerically prove $\epsilon_{M+1} = -I$ will probably never be sufficiently accurate to detect so small a difference. PL note that Laufer and Krieger⁸ have proven that $\epsilon_{KS} = -I$ for a Hooke’s atom, i.e., two electrons in a parabolic potential, which repel each other with a Coulomb potential. Two electrons are a special case because $\psi(r) = [\rho(r)/2]^{1/2}$ while the Hooke’s atom is a truly unique case. The wave function factorizes into a function of the center of mass coordinate and a function of the relative coordinate while $E(N=2) = E_{\text{cm}} + E_{\text{rel}} = 1.5k^{1/2} + E_{\text{rel}}$ and $E(N=1) = 1.5k^{1/2}$ where k is the Hooke’s law constant. Using the WKB approximation, $\psi(r)$ was obtained⁹ at large r and the KS equation inverted to obtain $\epsilon_{KS} = E_{\text{rel}}$

$=E(N=2) - E(N=1)$. One cannot conclude from this that $\epsilon_{M+1} = -I$ for potentials which do not allow the wave function to be factorized.

A simple proof that $\epsilon_{M+1} = -I$ goes as follows. For a pure state $v_{\text{KS}}(\mathbf{r})$ may always be chosen to vanish at infinity. Therefore its KS charge density which is identical to the many-body charge density decays as $\exp[-2(-2\epsilon_{M+1})^{1/2}]$ whereas the many-body charge density decays as $\exp[-2(2I)^{1/2}]$. The proof given in Ref. 2 that the many-body charge density decays as stated consists of writing the equation

$$[-\nabla^2 + v(\mathbf{r}) + v_{\text{eff}}(\mathbf{r})]\rho^{1/2}(r) = \mu\rho^{1/2}(\mathbf{r}) \quad (7)$$

where μ is defined to be $-I$, $v(\mathbf{r})$ is the external potential, $\rho(\mathbf{r})$ is the charge density of the exact many electron ground state $\psi(N)$, and $v_{\text{eff}}(\mathbf{r})$ is a potential they derive. [Note that their Eqs. (7) and (8), which state that μ is a Lagrange multiplier for the charge conservation condition, have nothing to do with their proof and are unlikely to be correct since there is no reason to expect that the Lagrange multiplier is $-I$ for a finite system.] The proof concludes by arguing that $v_{\text{eff}}(r \rightarrow \infty) \rightarrow 0$. This requires that

$$\varphi(N-1) = N^{1/2}\psi(N)/\rho^{1/2}(\mathbf{r}_N) \quad (8)$$

becomes equal to a combination of degenerate $\psi(N-1)$ ground states differing only in spin (spin-orbit coupling is completely neglected throughout) when $r_N \rightarrow \infty$. $\varphi(N-1)$ is

taken to be a $(N-1)$ electron wave function with \mathbf{r}_N and the spin of the N th electron treated as parameters. It is fairly obvious for transition metals whose principle Slater determinants contain $d^n s^2$ valence functions but whose ionic determinants contain $d^n / 1$ valence functions that $\varphi(N-1)$ does not collapse to the $\psi(N-1)$. Consider now a $s^2 p^3$ atom with S symmetry. $\rho(\mathbf{r}_N)$ is spherical so $\varphi(N-1)$ must have S symmetry (under rotation of all the electron coordinates and the parameter \mathbf{r}_N). Thus even as $\mathbf{r}_N \rightarrow \infty$, it is not possible for $\varphi(N-1)$ to collapse to the P symmetry of the $s^2 p^2$ ion. It is possible that $\varphi(N-1)$ collapses to a combination of the three degenerate P states with coefficients which depend on the direction in which $\mathbf{r}_N \rightarrow \infty$, so as to preserve the overall S symmetry under a rotation of all the coordinates and \mathbf{r}_N . Therefore, I conclude that for some cases, if not all, the proof fails. Furthermore, other proofs given in the literature contain unproven assumptions, according to the authors of Ref. 2. Therefore, except for the Hooke's atom, I assert that $\epsilon_{M+1} = -I$ remains unproven.

Note added in proof. PL appear to have added Appendix A to their Comment to refute my statement that there is no reason to expect that the Lagrange multiplier is equal to $-I$. They obtain $\mu = \partial E_N^g / \partial N$. But $\tilde{\rho}_N(\mathbf{r})$ is determined by ω , which brings us back to the original argument of Ref. 7 based on the nonarbitrariness of $\delta\tilde{\rho}_N$.

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